SOIL FUNCTION FOLLOWING REMEDIATION USING EX SITU THERMAL DESORPTION

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Peter Louden O'Brien

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Peter Louden O'Brien

The Supervisory Committee certifies that this ***disquisition*** complies with North Dakota State University's regulations and meets the accepted standards for the degree of

DOCTOR OF PHILOSOPHY

SUPERVISORY COMMITTEE:

Thomas DeSutter
Chair

Francis Casey

Abbey Wick

Eakalak Khan

Approved:

Nov 2, 2017	Francis Casey
Date	Department Chair

ABSTRACT

Soils perform many functions essential to human and ecosystem health, and contamination by organic compounds diminishes the ability of the soil to perform those functions. One method for remediating contaminated soils is ex situ thermal desorption (TD). This process involves excavating contaminated soil material and heating it to encourage contaminant vaporization. Gaseous contaminants are combusted in a thermal oxidizer, while the treated soil is available for reuse. While TD is a fast, reliable way to remediate contaminated soil, the ability of the soil to function after treatment is unknown. The aim of this research was to determine the viability of using TD-treated soil for agricultural production. Laboratory, greenhouse, and field experiments were conducted to compare soil properties of TD-treated soil to non-contaminated topsoil, as well as to explore the effects of mixing TD-treated soil with topsoil. Laboratory experiments found that soil organic carbon was diminished following treatment, which corresponded with an increase in saturated hydraulic conductivity and a decrease in aggregate stability. Despite these alterations, a greenhouse study found that wheat grown in TD-treated soils matched topsoil in producing mature wheat grain, but the grain was lower quality than that grown in topsoil. Further, the soil mixtures produced less grain than either material alone. These findings suggest that microorganism interactions affected the pool of nutrients available to the wheat, especially plant-available nitrogen. Under field conditions, the surface energy balance of TD-treated soils was similar to native topsoil, although the soil heat flux was slightly elevated. These findings indicated that soil temperature dynamics and evaporative fluxes are not different between TD-treated and native topsoil. Overall, this research suggests that TD-treated soils can be viable for agricultural production, but they are unlikely to match native topsoil in either production quantity or quality. Mixing TD-treated soil may mitigate some of the negative impacts of TD-treatment by reintroducing soil organic matter and biological communities, which could further enhance the rate of recovery of soil function.

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PREFACE

This dissertation describes research that was conducted following a crude oil spill on agricultural soil in western North Dakota. The spill, discovered in October 2013, was the result of a pipeline leak caused by a lightning strike. This leak released over 21,000 barrels of Bakken crude oil into an agricultural field producing durum wheat, and less than a quarter of that oil could be recovered. Bakken crude is a light, sweet oil that has very low viscosity and moves readily in the soil. Further, the spill occurred on soils formed from glacial till with highly heterogeneous subsurface material. These factors, in conjunction with the oil being under high pressure from the pipeline leak, caused the spill to move hundreds of meters laterally and up to 15 meters below the soil surface.

The remediation method chosen for this project was ex situ thermal desorption. This process involves excavation of contaminated materials, which are treated by passing them through a thermal desorption unit that heats the material and removes contaminants via vaporization. The gaseous contaminants are then combusted in a thermal oxidizer, while remediated soil is available for reuse. Thermal desorption is most efficient at treating contaminants comprised of more volatile compounds (like Bakken crude) with low boiling points, since lower temperatures are required to encourage vaporization.

While this method is a fast and reliable way to remove contaminants, the effects of thermal desorption on soil characteristics have not been fully explored. These effects are especially important in western North Dakota, where historically agricultural areas are now being exposed to high-density oil production. When crude spills occur in this region, remediation activities should allow for the return of the land to agricultural production. This agricultural production is not only vital to the long-term economy of the region, but also to the food security of the region and the nation.

The objective of this research is to determine if soils treated by thermal desorption are viable for use in agricultural production, with five chapters documenting a progressive acquisition and application of knowledge pertaining to thermal desorption-treated soils. Chapter 1 is a literature review compiling existing knowledge of the alterations to soil characteristics that occur after thermal treatment, which suggested possible concerns that may need to be addressed following remediation. Chapter 2 begins the site-specific research, with a laboratory study that focuses on soil physical and hydraulic properties following treatment of non-contaminated topsoil and subsoil using thermal desorption. Using the lab study to identify areas of concern, namely loss of soil organic matter, Chapter 3 describes a greenhouse study growing hard red spring wheat using remediated soils mixed with non-contaminated topsoil. Chapter 4 then describes the construction of large-scale field research plots directly adjacent to the ongoing remediation project. These plots incorporated a mixing technique to homogenously mix thermal-desorption treated soil and non-contaminated topsoil to mitigate the loss of soil organic matter and decreased biological activity identified in the laboratory and greenhouse studies. Chapter 5 describes the surface energy balance over the field research plots using micro-Bowen ratio instrumentation, which was used to quantify evaporative fluxes and soil temperature dynamics. These processes are critical to agricultural production in western North Dakota because of low seasonal precipitation and short growing seasons. Finally, the findings of all five chapters are incorporated into some general conclusions about soil properties and potential use after remediation using ex situ thermal desorption.

TABLE OF CONTENTS

CHAPTER 4. A LARGE-SCALE SOIL-MIXING PROCESS FOR RECLAMATION OF HEAVILY DISTURBED SOILS 70

CHAPTER 5. DAYTIME SURFACE ENERGY FLUXES OVER SOIL MATERIAL REMEDIATED USING THERMAL DESORPTION 93

LIST OF TABLES

LIST OF FIGURES

CHAPTER 1. THERMAL REMEDIATION ALTERS SOIL PROPERTIES – A REVIEW

Abstract

Contaminated soils pose a risk to human and ecological health, and thermal remediation is an efficient and reliable way to reduce soil contaminant concentration in a range of situations. A primary benefit of thermal treatment is the speed at which remediation can occur, allowing the return of treated soils to a desired land use as quickly as possible. However, this treatment also alters many soil properties that affect the capacity of the soil to function. While extensive research addresses contaminant reduction, the range and magnitude of effects to soil properties have not been explored. Understanding the effects of thermal remediation on soil properties is vital to successful reclamation, as drastic effects may preclude certain post-treatment land uses. This review highlights thermal remediation studies that have quantified alterations to soil properties, and it supplements that information with laboratory heating studies to further elucidate the effects of thermal treatment of soil. Notably, both heating temperature and heating time affect i) soil organic matter; ii) soil texture and mineralogy; iii) soil pH; iv) plant available nutrients and heavy metals; v) soil biological communities; and iv) the ability of the soil to sustain vegetation. Broadly, increasing either temperature or time results in greater contaminant reduction efficiency, but it also causes more severe impacts to soil characteristics. Thus, project managers must balance the need for contaminant reduction with the deterioration of soil function for each specific remediation project.

Introduction

Soil contamination by organic compounds affects thousands of sites across the United States, and many different land uses (USEPA, 2014). Organic contaminants can be directly toxic to biological organisms (Ramadass et al., 2015; Eom et al., 2007), so the functioning of both natural (Robson et al., 2004) and agricultural systems (Issoufi et al., 2006) can be altered. Additionally, this contamination may be a risk to human health (Ruby et al., 2016), which precludes residential or commercial use of these areas. Further, the contamination may migrate through air, soil, or water to affect a much broader area than the original contamination. Thus, remediation techniques may be required to quickly return the contaminated areas to previous land use and mitigate risk to human and ecosystem health.

Many types of methods for soil remediation are available (Lim et al., 2016; Khan et al., 2004), including biological, physico-chemical, thermal, and integrated strategies, and the most appropriate method is a project-specific determination. While not applicable in all situations, thermal remediation offers greater control over operational parameters (e.g., heating time, temperature) and is used when goals include i) fast removal of contaminants; ii) strict adherence to a cleanup goal, requiring high reliability; and iii) reduction of long-term liability (Vidonish et al., 2016b). Thermal remediation is a category of techniques that use the application of heat to i) enhance the mobility of contaminants (e.g., steam/hot air injection); ii) separate contaminants from soil particles (e.g., thermal desorption, microwave heating); iii) transform contaminants into less toxic byproducts (e.g., pyrolysis); iv) destroy contaminants (e.g., incineration, smoldering); or v) immobilize contaminants (e.g., vitrification) (FRTR, 2017).

While thermal treatment can be faster and more reliable than some other methods, it typically requires more infrastructure and machinery, resulting in higher costs. Additionally, soil heating is known to affect numerous soil properties (Sierra et al., 2016; Yi et al., 2016; Pape et al., 2015), and the alteration of these properties may dictate land use following remediation. The extent of this alteration may be an important factor in the implementation of thermal remediation, as many practitioners are pairing remediation with subsequent reclamation or restoration efforts (Wagner et al., 2015). Thus, understanding the effects of thermal remediation on soil properties is critical information in the decision-making process that occurs at the beginning of a project. Extensive research has been conducted pertaining to the optimization of these techniques and the applicability across a range of situations (Gao et al., 2013; Thuan and Chang, 2012; Aresta et al., 2008). However, this research often ignores the impacts of thermal treatment on the remediated soil, so a comprehensive examination of the magnitude of the effects and their implications on soil function is needed (O'Brien et al., 2017a).

Connecting the effects of thermal remediation to soil function is vital in the subsequent reclamation or restoration process (Farag et al., 2015). Soil function, in this review, is understood as the ability of the soil to perform the following functions: i) serve as suitable habitat capable of sustaining biodiversity; ii) provide structure and a resource medium for biomass production; iii) store and filter water resources; iv) degrade, detoxify, and manage wastes through nutrient cycling and long-term resource storage; v) act as an engineering medium for human development; and vi) provide cultural and anthropological significance (Bone et al., 2010). The aims and circumstances of each project determine how the effects to soil function may be relevant in long-term project management (Ehrenfield, 2000). For example, some projects may be aimed at returning the land to commercial or industrial use, so potential productivity of the soil may be a low priority. However, soil strength and stability are essential when utilizing it as an engineering medium. Conversely, remediation projects on agricultural land or natural areas may have a goal of restoring the land to a pre-disturbance state, so reclamation goals may focus on the functions of providing habitat, biomass production, water management, and nutrient cycling.

Due to limited literature describing soil properties following thermal remediation, some wildfire research has been included in the review. Since the goal of thermal remediation is to create predictable, uniform heating, wildfire research conducted under field conditions is not applicable because it has widely variable heating conditions. Vegetation, litter depth, topography, soil water content, and soil pore networks are so variable across space and depth that heating time and intensity cannot be uniform within the soil profile (Busse et al., 2010; Archibold et al., 1998; Campbell et al., 1995). Only wildfire research that incorporated laboratory heating to simulate fire conditions may mimic conditions found in some remediation projects, so those studies are included in the review. Additionally, this review does not include any research that separates soil fractions (e.g., sand-sized particles) before heating, since soils are not separated by particle size prior to thermal remediation.

This review aims to examine the impacts of several thermal remediation techniques on soil properties and discuss the importance of those impacts in the context of contaminated site management. This assessment begins with a discussion of the principles of thermal remediation, and the most common thermal remediation heating times and temperatures are identified. Then, the direct impacts of thermal remediation to several individual soil characteristics are explored, with special emphasis on literature from remediation research projects. This information is supplemented by laboratory heating studies that elucidate the effects of heating on each property. Finally, the importance of these impacts in the implementation of remediation and reclamation strategies is discussed.

Thermal Remediation for Contaminant Reduction

Pathways for thermal remediation

Thermal remediation can be applied to both surface- and sub-soil materials to reduce a range of organic contaminants, including petroleum hydrocarbons (PHC), polycyclic aromatic hydrocarbons (PAH), polychlorinated biphenyls (PCB), and pesticides (Figure. 1a); additionally, thermal treatment is effective at reducing mercury concentration in soils. The four pathways for thermal remediation addressed in this review are i) enhanced mobility, ii) separation, iii) transformation, and iv) combustion (Vidonish et al., 2016b). A fifth pathway, immobilization, is possible through vitrification (Khan et al., 2004), but it is less common and forms a product that cannot be used as soil, so it is outside the scope of this review. Additionally, low temperature heating (< 100 °C) can encourage increased biological degradation (Zeman et al., 2014), but it does not directly reduce contaminant concentration, so thermally enhanced biodegradation is also omitted from the review.

Enhanced mobility refers to using thermal treatment to increase the rate of removal of organic contaminants, typically in vapor phase. Methods that employ enhanced mobility, such as hot air injection or steam injection (Tzovolou et al., 2011; Schmidt et al., 2002), are typically applied in-situ, and they are akin to air sparging and soil vapor extraction (FRTR, 2017). This method recycles warm (up to 250 °C), non-contaminated air/steam through the contaminated zone in order to encourage vaporization, and it is typically limited to hydrocarbons with low Henry's constant values or low boiling points (< 250 °C). The vapors that are cycled through these injection systems are then contained for either recovery or further treatment.

Similar to enhanced mobility, the separation pathway involves removing vapor phase contaminants. While enhanced mobility applies heat to encourage extraction of contaminants in vapor phase, separation applies heat to cause contaminants to transition into vapor form. Thus, separation requires higher temperatures (250 °C – 550 °C) to reach the boiling point of contaminants in order to separate the vapor phase contaminant from the solid phase soil matrix via vaporization (Lighty et al., 1990). The most common method of remediation that utilizes separation is thermal desorption (e.g., Aresta et al., 2008), although separation can also be induced via microwave heating (Falciglia and Vagliasindi, 2015). Enhanced mobility and separation can be applied simultaneously, wherein in-situ thermal desorption separates contaminants from the soil matrix and an associated heated air vacuum system removes the vapors (Vidonish et al., 2016b). Typically, however, enhanced mobility is employed with an in-situ treatment method, whereas separation is attained using an ex-situ treatment method.

The transformation pathway involves the chemical decomposition of contaminants, which is most often achieved by heating contaminated material in the absence of oxygen (i.e., pyrolysis; Vidonish et al., 2016a). This process creates a highly carbonaceous product called char or biochar, as chemical bonds of the contaminants break to form free radicals and undergo aromatic condensation reactions (Vidonish et al., 2016a). Since this process requires an anoxic environment, it is typically applied with an ex-situ treatment method. The transformation mechanism to form char is commonly used during remediation of hydrocarbons, but it may also be applied to other organic compounds, such as pentachlorophenol (Thuan and Chang, 2012). However, the composition of the char is dependent on the characteristics of the materials (both contaminant and soil) that undergo pyrolysis.

The combustion pathway involves exposing the contaminant to enough energy to break the molecular bonds, accompanied by an oxidation reaction to form less hazardous materials. For example, hydrocarbon combustion primarily produces CO_2 and H_2O, while chlorinated compounds may produce HCl and Cl_2. Combustion requires much higher temperatures than separation (up to 1000 °C), and the most common form of this technique is soil incineration, although it also occurs during smoldering remediation (Pape et al., 2015). Additionally, the by-products of incomplete combustion of PAHs, PCBs, and polychlorinated dibenzodioxins/furans can be hazardous (Sato et al., 2010; Risoul et al., 2005), so caution needs to be applied to avoid the creation of those compounds.

In practice, many thermal remediation techniques employ multiple of these four pathways, but each technique has particular contamination circumstances to which it is best suited. Generally, these pathways follow a sequential relationship with temperature, wherein enhanced mobility requires heating to the lowest temperature, while combustion requires the highest heating temperatures. However, the goal of remediation is not to expose contaminated soils to each of the pathways but rather to optimize contaminant reduction through whichever pathway is most efficient. Thus, the preferred pathway for a given remediation project varies depending on the type of contaminants present, because contaminant properties (e.g., boiling point) dictate the most appropriate heating times and temperatures.

Table 1. Thermal treatment studies applied to contaminated soils based on contaminant. Studies are shown with pre- and post-treatment contaminant concentrations, heating time and temperature, and percent contaminant reduction. Many studies incorporated a variety of operating conditions, so ranges for these values are given.

Author	Concentration†	Time (min)	Temperature (°C)	End concentration†	% reduction*
		Polychlorinated biphenyls			
Aresta et al., 2008	1739	60	150 - 350	70 – 1739	0 – 96
		5 – 150	300	35 – 1739	0 – 98
Qi et al., 2014	500	60	300 - 600	10 -180	64 - 98
Risoul et al., 2002	50	30	150 - 450	0.5 – 50	0 -99
Sato et al., 2010	11	5	400	3 – 6	48 - 70
Zhao et al., 2012	8.2	5	450	0.1	99
		Petroleum hydrocarbons, including polycyclic aromatic hydrocarbons			
McAlexander et al., 2015	40867	60	340 - 430	409 – 817	98 - 99
Tatano et al., 2013	49933-81137	60 – 90	300	499 – 732	99
		60 – 90	350	668 – 811	99
Vidonish et al., 2016a	15000	180	420 - 650	90 – 200	99
	19000	180	420 - 650	170 – 340	99
Wang et al., 2010	8200	10 – 90	225	2130 – 4100	50 – 74
		10 – 90	325	492 – 3772	54 – 94
		10 – 90	400	82 – 1968	76 – 99
		10 – 90	500	82 – 410	95 – 99
Yi et al., 2016	5133	15	200	255	95
		Mercury			
Huang et al., 2011	180	60	120 - 550	4 – 189	-5 – 98
	767	60	170 - 550	8 – 491	36 – 99
	1320	15 – 240	250 - 550	0 – 436	67 – 100
Ma et al., 2014	69	20	100 - 700	.67 – 64	7 – 99
Sierra et al., 2016	35	60	60 - 750	.35 – 27	23 – 99
	10497	60	60 - 750	105 - 7558	28 – 99
		Pesticides			
Gao et al., 2013	BHC/DDT: 3116	10 – 90	225	779 – 1932	75 – 38
		10 – 90	325	156 – 1340	57 – 95
		10 – 90	400	32 – 935	70 – 99
		10 – 30	500	0.3 – 189	94 – 99
Sahle-Demessie and Richardson, 2000	DDT: 5085	30	350	51	99
	DDD: 2047	30	350	20	99
	DDT: 115	30	350	21	82
		Pentachlorophenol			
Thuan and Chang, 2012	91	10 – 60	200	72 – 75	18 – 20
		10 – 60	250	49 – 52	40 – 46
		10 – 60	300	15 – 27	70 – 83
		10 – 60	350	5 – 8	92 – 95
		Polychlorinated dibenzo-p-dioxins and dibenzofurans			
Troxler et al., 2010	33 μg kg^{-1}	variable	450 - 550	0.33 - 1.65 μg kg^{-1}	95 -99
Lee et al., 2008	36	60	750 - 850	0-0.004	99 – 100

† Units may be approximated or rounded from original publication; unless otherwise stated, units for concentration pre- and post-treatment are in mg kg^{-1}

* % Reduction calculated by the equation: 1 – (Concentration$_{\text{final}}$ / Concentration$_{\text{initial}}$) using mean values extracted from each study.

BHC: β-hexachlorocyclohexane; DDT: Dichlorodiphenyltrichloroethane; DDD: Dichlorodiphenyldichloroethane

Application of thermal remediation

Given the range of temperatures used in remediation (Table 1), as well as the risks associated with incomplete remediation or the creation of hazardous compounds, determining the appropriate heating conditions is vital. Two conditions manipulated in thermal remediation are heating temperature and heating time. Ensuring that contaminated soils reach the appropriate temperature to remove the contaminant is often difficult because of the thermal properties of soil. Soil is a heterogeneous matrix, and heat transfer is not uniform due to the variability in pore sizes, water content, and composition of the solid materials (Lu et al., 2014). Soils with high water content, porosity, and soil organic matter (SOM) have lower thermal conductivity than dry, dense mineral soils (Abu-Hamdeh and Reeder, 2000), so more energy is required to heat materials evenly within those soils, requiring either higher temperatures or longer heating times. For this reason, thermal remediation often employs pretreatment of drying the soil and breaking it into smaller pieces to make the heating more efficient.

Removal efficiencies for a single contaminant under the same heating conditions can vary greatly (Table 1) due to soil thermal properties. Table 1 shows information extracted from 18 thermal remediation studies of contaminated soils, including the range of heating temperatures and heating times applied to reduce several different contaminant types, as well as the effectiveness of those heating regimes to reduce contaminant concentration. The variability in contaminant reduction identified in Table 1 demonstrates the importance of understanding site-specific characteristics on remediation, such as soil texture, mineralogy, or soil water content. Accordingly, these characteristics determine the optimal heating conditions for thermal remediation, which, in turn, determine the impacts to soil properties.

For example, certain heating time and temperature are required to remediate diesel fuel from a wet, high SOM soil. Applying those same conditions to remediate diesel fuel from a dry soil with low SOM would likely exceed what is necessary for contaminant reduction, which would increase project energy costs and result in more severe impacts to soil properties. Conversely, applying the energy required to reduce contaminants of the dry, low SOM soil would not be sufficient to remove all contamination in the wet, high SOM soil, resulting in persistence of contamination and possible liability risks to remediation practitioners. Thus, active monitoring of ongoing remediation projects is required to best provide assurance of contaminant reduction without excessive application of heating time or temperatures.

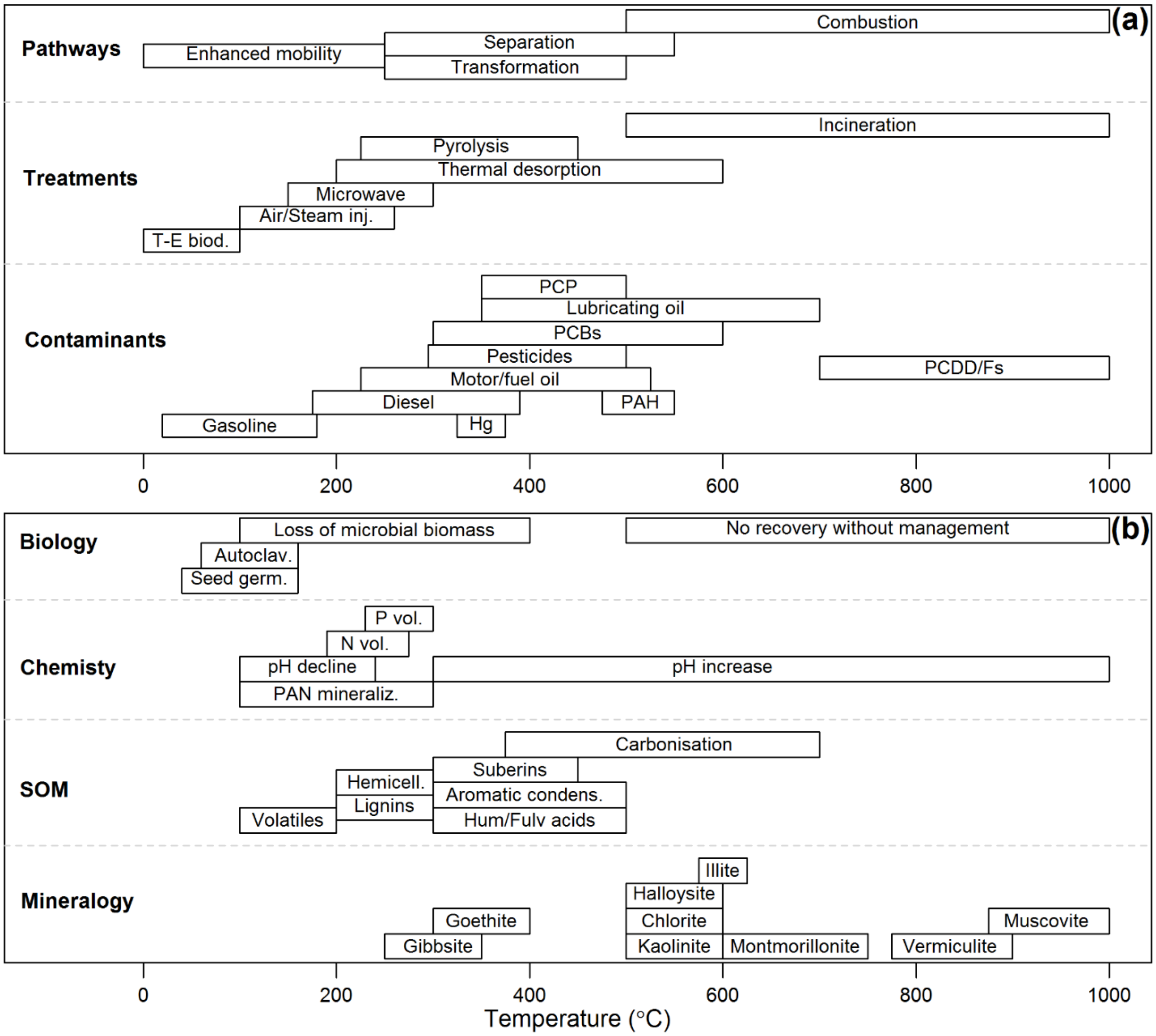

Figure 1. Range of heating temperatures associated with common pathways and thermal remediation methods, as well as range of temperatures typically applied to various organic contaminants in soil (Panel (a)). Panel (b) shows the temperatures at which soil biology, chemistry, soil organic matter (SOM), and clay mineralogy are affected. For biology, the bars represent temperatures at which organisms are inhibited. For SOM and mineralogy, the bars indicate the range of temperatures at which each component (SOM) or specific mineral (Mineralogy) degrades.

Effects of Soil Heating on Soil Properties

Determining the overall effect of soil heating on soil functions cannot be directly measured because those functions are governed by the dynamic interactions of many different soil properties and environmental processes. Nonetheless, identifying changes to specific soil properties is valuable in making assumptions about how overall soil function will be affected by heating (O’Brien et al., 2017a).

Soil organic matter

Thermal treatment of soil inevitably results in degradation of SOM, as the temperatures required to remediate contaminants exceeds the temperatures at which most components of SOM remain stable. Notably, SOM is reduced through thermal remediation by three mechanisms: 1) volatilization of some constituents (distillation); 2) transformation and condensation (charring); and 3) oxidation (combustion) (Certini, 2005). The extent of degradation is dependent on the composition of the SOM, as these mechanisms interact differently with each constituent of SOM (Figure 1b; Kiersch et al., 2012). The distillation of volatile constituents and the degradation of lignins and hemicellulose occur between 100 – 200 °C, while the decarboxylation of humic and fulvic acids does not occur until heating above 300 °C (Gonzalez-Perez et al., 2004). Finally, heating above 500 °C volatilizes all alkylaromatics, lipids, and sterols (Schulten and Leinweber, 1999) and causes carbonization to occur (Kiersch et al., 2012). Thus, in addition to reducing overall amount of SOM, thermal remediation can alter the structure of the remaining SOM, resulting in more condensed, aromatic structures (Kiersch et al., 2012; Biache et al., 2008; Gonzalez-Perez et al., 2004).

In practice, these mechanisms of SOM decomposition result in a wide range of SOM reduction in remediation projects based on heating time and temperature. For projects requiring lower heating intensities, such as heating at 200 °C for 15 min, SOM reduction may only be about 10% (Yi et al., 2016). Conversely, incineration projects that involve heating to 620 °C for 180 min can reduce SOM by more than 90% (Vidonish et al., 2016a), and smoldering remediation for 60 min can almost entirely remove SOM (Pape et al., 2015). More commonly, however, soil remediation of organic contaminants occurs for between 30 and 60 min at temperatures from 300 – 400 °C. With these heating conditions, SOM reduction can range 35-40% (Ma e al., 2016; Tatano et al., 2013, Huang et al., 2011) to 80% (Sierra et al., 2016).

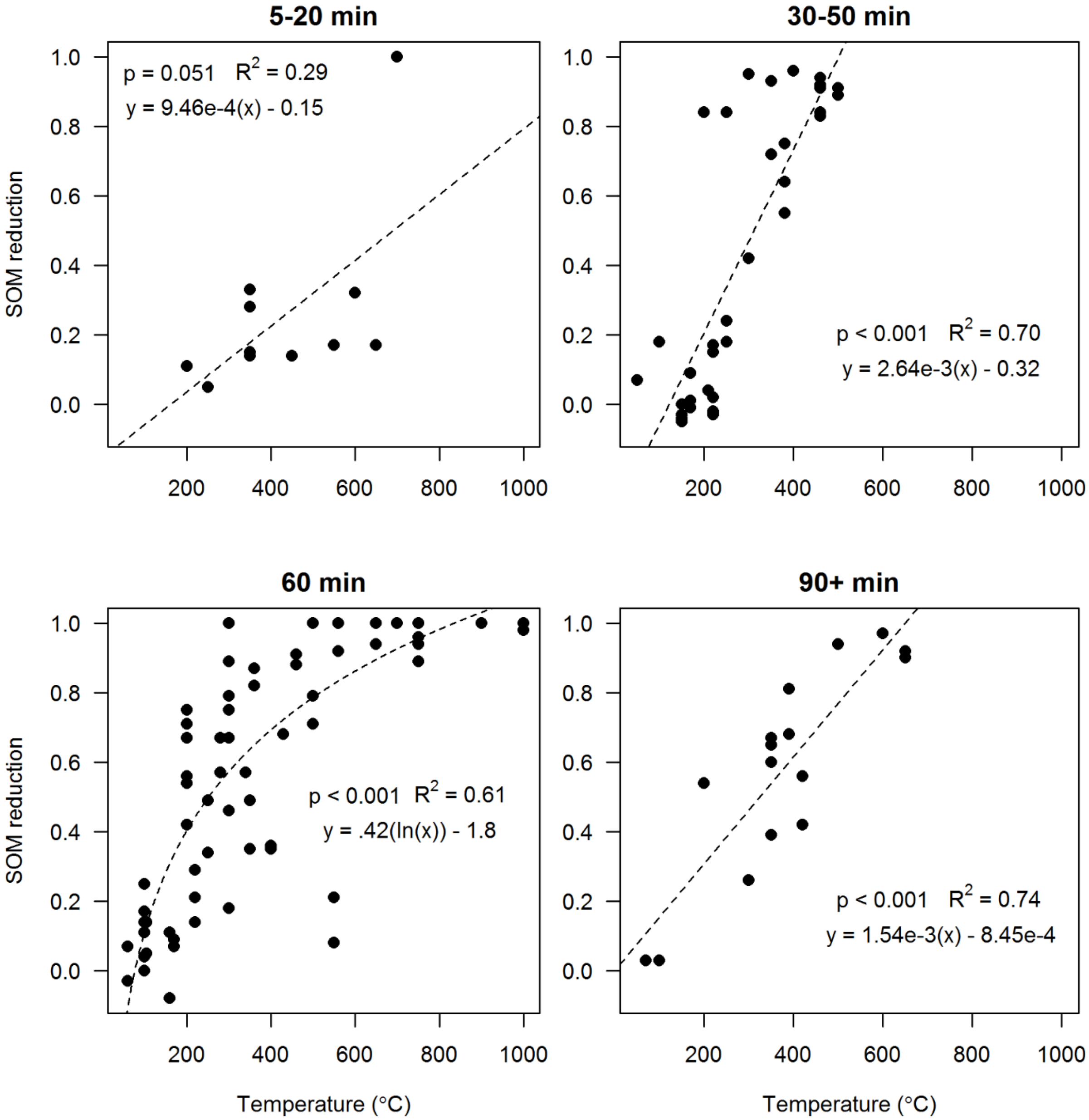

Figure 2. The reduction of soil organic matter (SOM) across a range of temperatures, with each panel corresponding to heating duration. Each point represents a mean value from the reported literature, with 135 data points extracted from 19 different studies. Reduction values were calculated by the equation: 1 – (SOM_{final} / $SOM_{initial}$).

Despite the variability in SOM reduction, some trends are evident in Figure 2, which includes mean SOM data pre- and post- soil heating extracted from 19 different studies, including both contaminated and non-contaminated soils. When heated to temperatures at or below 300 °C, SOM is not greatly reduced, even as time increases. However, increasing heating time at temperatures above 300 °C can drastically reduce SOM. For example, when heating a sandy loam at 300 °C, the differences between 60 min (19%) and 90 min (25%) were minimal. However, at 350 °C, the differences between 60 min (35%) and 90 min (65%) were much greater (Tatano et al., 2013). Notably, in 53 of the 60 cases included in this review, SOM was reduced by greater than 50% when heating at and above 350 °C for longer than 20 min.

Soil texture and mineralogy

Thermal remediation can cause changes to soil texture and mineralogy because mineral clay lattice structures can become dehydrated and break down under excessive heating (Borchardt, 1989; Dixon, 1989; Fanning, 1989). Following this decomposition of mineral structure, the amorphous clay-sized particles are cemented together by Fe- and Al-hydroxides released during the combustion of SOM (Ketterings et al., 2000), resulting in larger particle sizes. Each specific mineral has a temperature threshold at which this dehydoxylation occurs (Figure 1b), so soil mineralogy dictates how much clay breaks down during heating. Kaolinite structures generally begin to deteriorate when heated between 420 °C and 500 °C (Dixon, 1989), while montmorillonite lattice structure remains stable until heated above 700 °C (Borchardt, 1989). Micas show a large range of resistance to soil heating, as dehydroxylation of illites begins above 550 °C, but muscovites do not breakdown until heated above 940 °C (Fanning, 1989).

Due to these high temperatures required to break down mineralogy, large textural shifts associated soil heating generally do not occur at temperatures below 400 °C (Pape et al., 2015; Terefe et al., 2008), even when exposed to heat for up to 6 h (Kang and Sajjapongse, 1980). Figure 3a shows how this 400 °C threshold manifests across in the relative reduction of clay-sized particles (< 0.002 mm) found in nine soil heating studies. Some reductions in clay-sized particles occur between 350 and 400 °C, with none greater than 50%. However, of the 24 soil samples that were heated above 400 °C, 21 had greater than 60% reduction of clay-sized particles.

At heating temperatures above 400 °C, the reduction of clay-sized particles is typically accompanied by an increase of percentages of sand-sized particles (0.05 mm – 2 mm) due to cementation. For example, two Italian alluvial soils decreased in clay-sized particles from 48% to 8% and 11% to 4%, respectively, when heated at 460 °C for 60 min (Giovannini et al., 1988). Soils taken from active remediation sites utilizing thermal remediation at less than 400 °C did not find changes in particle size distribution (O'Brien et al., 2016; Ma et al., 2014; Roh et al., 2000). However, increasing the heating temperature of PHC-contaminated soils to 600 °C for 10 min reduced percentage of clay-sized particles from 32% to 12%, while sand-sized particles increased from 21% to 65% (Roh et al., 2000). This soil also shifted from a mixed mineralogy of kaolinite and illite pre-heating to only illite post-heating, likely due to the different heat thresholds of these minerals (Figure 1b). Another Hg-contaminated soil from China had a less dramatic decrease in clay-sized particles, from 31% to 20%, despite being heated to 700 °C for 20 min (Ma et al., 2014). Differences between studies are likely the result of different heating times and clay mineralogy of the samples.

Some exceptions to the 400 °C threshold do exist. Badia and Marti (2003) found a decrease in clay-sized particles from 32% to 17% after heating at only 250 °C for 60 min, which corresponded with an increase in sand-sized particles from 23% to 31%. Additionally, heating at higher temperatures does not always alter particle size distribution, as a study on soil from Taiwan found heating up to 550 °C for 60 min did not change particle size distribution, which was likely due to the small fraction of kaolinite and the method of heating (Huang et al., 2011). Since this study used indirect heating and an oxygen-deprived environment, very little SOM was lost. Thus, the cementing agents, typically formed from transformed SOM, were not available to fuse any of the smaller sized-particles together.

Soil pH

Soil pH changes during thermal remediation projects are also governed by heating time and temperature (Figure 3b). In many cases, especially at lower temperatures (< 250 °C), soil pH is unchanged or slightly decreases with thermal treatment. This decrease is likely caused by some oxidation reactions, as well as the formation of HCO_3^- following the mineralization of CO_2 associated with soil heating (Sierra et al., 2016; Ma et al., 2014; Badia and Marti, 2003; Roh et al., 2000). However, heating above 250 °C leads to the combustion of SOM and subsequent pH increase by two mechanisms. First, organic acids are destroyed, removing their acidifying influence from the soil solution (Pape et al., 2015; Terefe et al., 2008). Second, the higher temperatures and dehydration of soil colloids displaces H^+ and replaces them with alkali cations, which are abundant in soil solution following combustion of SOM (Sierra et al., 2016; Terefe et al., 2008; Badia and Marti, 2003). Thus, soils with higher SOM are likely to have greater changes in pH following thermal treatment. Conversely, pH shifts are less pronounced in soils with low SOM or high $CaCO_3$ contents, as $CaCO_3$ buffers against pH changes and requires very high temperatures before decomposition.

These trends have been found in active remediation projects, where heating mercury contaminated soils for 60 min at temperatures between 60 °C and 220 °C resulted in pH decreases from 6.9 to 6.1 (Sierra et al., 2016) However, Yi et al. (2016) found no change in pH heating at 200 °C for 15 min. At higher temperatures, 350 °C, used in a thermal desorption study, pH increased from 7.3 to 7.7 when heated for 10 min, while it increased further to 8.2 when heated to 600 °C for 10 min (Roh et al., 2000). Similarly, O'Brien et al. (2017b) found pH to increase from 7.4 to 8.2 after heating at 350 °C for 10 min. The largest pH increase identified in this review went from 5.2 to 9.8, and resulted from treatment at 700 °C for 20 min (Ma et al., 2014).

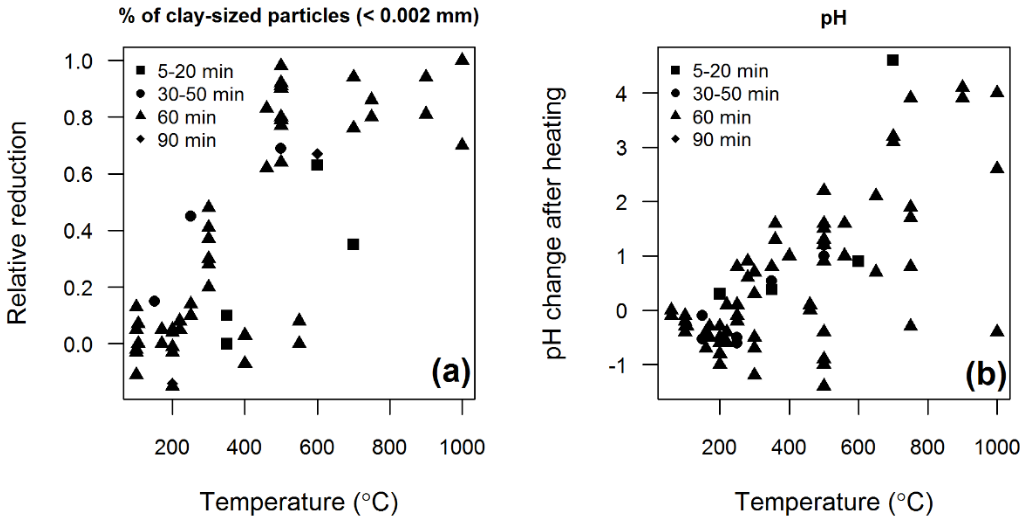

Figure 3. The relative reduction of clay-sized particles (< 0.002 mm; panel A) and pH change following soil heating (panel B). Heating times are signified by different shapes. Each point represents a mean value from the reported literature, with clay data comprising of 58 data points reported in nine different studies and pH data comprising of 90 data points reported in 13 different studies. Reduction values were calculated by the equation: 1 – (CSP_{final} / $CSP_{initial}$), where CSP: clay-sized particles.

Plant available nutrients and metals

The alteration of the SOM with thermal treatment of soil also alters the plant available nutrients and elements. Notably, the combustion of SOM leads to the loss of both C and N via volatilization (Yi et al., 2016; Giovannini et al., 1990). However, at lower temperatures (< 220 °C), soil heating can cause mineralization of organic N into both NO_3^- and NH_4^+, predominantly NH_4^+ (Glass et al., 2008). This transformation is not accompanied by a loss of total N until temperatures are above 220 °C (Glass et al., 2008; Giovannini et al., 1990). Soil P is more resistant to heating, and it often increases following soil heating (Yi et al., 2016; Galang et al., 2010). This increase is also the result of mineralization of organic P into inorganic P, as volatilization of P occurs at much higher temperatures than C or N. However, in some cases, plant available P interacts with the formation of new, more reactive minerals following rehydroxylation, which may sorb more P and reduce the plant-available fraction (Yusiharni and Gilkes, 2012).

Very few thermal remediation studies include discussion of plant available nutrients, so most information regarding these dynamics is found in laboratory heating literature. Generally, plant available nutrients decline with thermal treatment, corresponding to the loss of SOM. Thus, low temperature heating (e.g., 200 °C) did not decrease total N (Yi et al., 2016), but heating at 350 °C decreased total N from 2.2 g kg^{-1} to 1.6 g kg^{-1}, and heating at 600 °C decreased it further to 0.7 g kg^{-1} (Roh et al., 2000). Conversely, Vidonish et al., (2016a) found that pyrolysis at 420 °C more than doubled total N and plant-available P in one soil, but the same treatment decreased total N by 45%, and plant available P by 80% in another soil. Total N and P are heavily reduced following incineration at 650 °C (Vidonish et al., 2016a), and they are almost entirely depleted after smoldering treatment (Pape et al., 2015).

Soil heating has variable effects on heavy metals in the soil. One study found that heating at either 350 °C or 600 °C resulted in drastically increased plant available Fe and Al contents (Roh et al., 2000). While in other instances, the total amount of plant available metals remained unchanged after heating, but the fractionation shifted (Bonnard et al., 2010; Biache et al., 2008). No remobilization of metals occurred following heating at 500 °C, and several metals had increased residual fractionation, indicating that they will be less mobile and less bioavailable (Biache et al., 2008). However, other studies have identified an increase in genotoxicity due to heavy metals, suggesting that they were more bioavailable following treatment (Bonnard et al., 2010).

Soil biological communities

Generally, soil heating is detrimental to microorganisms, as evidenced by the fact that it is common practice to heat soils to destroy pathogens or unwanted bacteria or fungi (Wollum II, 1982). Notably, this heating occurs at much lower temperatures (e.g., 50 – 125 °C) than most thermal remediation techniques (Lobmann et al., 2016; van der Voort et al., 2016), and it does not sterilize the soil, but rather it eliminates certain target organisms. Thus, total soil microbial biomass can persist in field conditions heated up to 200 °C (Acea and Carballas, 1999). Fungi and bacteria are resistant to even higher temperatures in some cases, as they can survive after heating up to 300 °C – 400 °C (Barcenas-Moreno and Baath, 2009). However, other studies report declines in both bacteria and fungi at heating < 300 °C (Guerrero et al., 2005).

Although soil organisms decline immediately following heating, their recovery can be rapid, occurring after only a few days after heating to less than 300 °C (Barcenas-Moreno and Baath, 2009). Conversely, recovery may not happen after more extreme heating (300 °C and higher) for more than 100 days (Guerrero et al., 2005) or even more than 270 days (Badia and Marti, 2003). At temperatures above 500 °C, however, microbial activity may not recover without additional soil management, such as fertilizer or organic amendments (Pape et al., 2015). Similarly, soil microbial activity, as measured by dehydrogenase and beta-glucosidase, was reduced following thermal desorption at 250 °C for 15 min (Yi et al., 2016). These metrics may be also expected to recover, as Wang et al. (2010) found that dehydrogenase, invertase, and urease all recovered following the thermal treatment of PHCs at a range of temperatures up to 500 °C. Despite this some recovery, these metrics may not match untreated soil without additional management (Gao et al., 2013).

Further, the soil biological community composition changes following heating, wherein it displays greater diversity and favors heat-tolerant species (van der Voort et al., 2016). Overall, the ability of these organisms to recover is dependent on the conditions of the soil following treatment, such as SOM, available nutrients, and water content. Additionally, organisms must be reintroduced to the heated soil in some way, since most organisms are destroyed in the heating process. This reintroduction can be through wind or water deposition, but some researchers have inoculated thermally treated soil with un-heated soil to reestablish those communities (O'Brien et al., 2017c; Wang et al., 2010; Marschner and Rumberger, 2004).

Vegetation

The impacts of thermal remediation on vegetation can be assessed in two ways. First, the seedbank that is present during the remediation can be assessed for germination to determine how the treatment affects seed mortality. Similar to how soil heating is used to ‘sterilize’ soil of certain microorganisms and pathogens, the same process is often used to kill weed seeds from a seedbank. Thus, many seeds will be destroyed by thermal treatment at even the lowest temperatures. For example, weed seeds can be destroyed after exposure to temperatures below 100 °C for 5 min or less (Ribeiro et al., 2013; Ruprecht et al., 2013). However, response of seed germination to heating is variable depending on species. While germination of many graminoid species is hindered by heating at a range of temperatures below 300 °C, some *Fabaceae sp.* are positively affected by the heating (Ruprecht et al., 2013). Additionally, the conditions of the heating can dictate the effects of the seeds. For example, some pine species rely on fire to induce germination when the seeds are in the cone, but when the seeds are directly exposed to heat, the germination percentage rapidly reduces above 160 °C (Moya et al., 2013).

The second method for assessing plant response to thermal remediation is quantifying vegetative growth after the soil has been replaced. In this case, biomass production is informed by the alterations discussed above, namely SOM, texture, pH, plant available nutrients, and soil biological communities. Generally, these alterations to soil properties increase with increased heating time and temperature (e.g., Figure 2), so vegetative production is lower as heating temperatures increase (Pape et al., 2015). Notably, many studies have shown that thermally treated soils produce more biomass than contaminated soils (Ourvrard et al., 2011; Dazy et al., 2009; Roh et al., 2000), however, they do not match non-contaminated soils (O’Brien et al., 2017b; Vidonish et al., 2016a; Yi et al., 2016).

Implications

Figure 1 shows the relationship between common thermal remediation techniques and impacts to soil properties. While the exact temperature ranges may shift based on site-specific characteristics, the ranges offer a good general idea of how thermal treatment has varying effects on soil properties based on heating temperature. These impacts to soil properties (Figure 2, Figure 3) affect the ability of the soil to function. For example, reduced SOM is associated with lower biological activity, reduced nutrient cycling (Badia and Marti, 2003), and reduced aggregate stability (Six et al., 1998). Similarly, the degradation of clay mineralogy results in lower CEC and lower water holding capacity. Additionally, the transformation of SOM to have condensed, aromatic structures at lower temperatures results in hydrophobicity (Garcia-

Corona et al., 2004). These changes all adversely affect the ability of the soil to sustain both microorganisms and vegetation.

Finding the balance between the need for contaminant removal to avoid health risks and the damage to soil function must be done on a project-by-project basis, in accordance with site-specific conditions and project goals. In most cases, contaminant reduction takes first priority because of regulatory requirements and company liability concerns. However, the impacts to soil function should not be ignored, as subsequent reclamation or restoration efforts can be greatly affected by thermal remediation (Burger et al., 2016).

One difficulty in finding the balance between contaminant reduction and the changes to soil properties is that no absolute thresholds exist for how much change is too much for any given soil property. Given this difficulty, as well as the variability in post-remediation land use, the best approach is to compare pre-remediation soil properties with post-remediation values to determine the actual changes in each situation. Even with this approach, the balance remains subjective and must be determined by each specific project manager. Nonetheless, by understanding how soil properties are affected by thermal remediation, costs can be reduced and overall project times can be shorter. Understanding the appropriate heating temperature and time avoids excessive energy consumption without any benefit, and it minimizes the impacts to soil properties. Additionally, by understanding the effects to soil properties, even if those effects are unavoidable, project managers may plan accordingly for appropriate reclamation and restoration strategies.

Conclusions

Thermal remediation is effective at reducing contaminant concentrations, but it can also alter the ability of soil to function. For the most cost-effective and efficient remediation projects, these two consequences must be balanced. Optimum heating time and temperature are variable across the different types of contaminants, and increasing either time or temperature causes soil characteristics to deteriorate. Below 220 °C, soils are not greatly affected by short duration (e.g., less than 1 h) heating, although biological communities are diminished in the short term. However, above 220 °C, SOM decreases and may transform into a hydrophobic condensate. When temperatures increase about 300 °C, SOM decreases rapidly, increasing soil pH and altering nutrient availability, which causes diminished plant and microbial biomass production. Temperatures above 450 °C show great declines in SOM after heating for only 30 min. Additionally, soil mineralogy begins to collapse and soil particle size distribution shifts to become predominantly sand-sized particles. Along with these changes, pH increases dramatically and available nutrients decrease sharply to create inhospitable conditions for both plants and soil microorganisms. This deterioration may not be avoidable in all cases, but it should be taken into account for the overall project costs, as reclamation must address these issues before the projects are complete. Thus, planning for these effects should create reclamation projects that are cheaper, more efficient, and more successful.

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CHAPTER 2. IMPLICATIONS OF USING THERMAL DESORPTION TO REMEDIATE CONTAMINATED AGRICULTURAL SOIL: PHYSICAL CHARACTERISTICS AND HYDRAULIC PROCESSES[1]

Abstract

Given the recent increase in crude oil production in regions with predominantly agricultural economies, the determination of methods that remediate oil contamination and allow for the land to return to crop production is increasingly relevant. Ex situ thermal desorption (TD) is a technique used to remediate crude oil pollution that allows for reuse of treated soil, but the properties of that treated soil are unknown. The objectives of this research were to characterize TD-treated soil and to describe implications in using TD to remediate agricultural soil. Native, noncontaminated topsoil and subsoil adjacent to an active remediation site were separately subjected to TD treatment at 350°C. Soil physical characteristics and hydraulic processes associated with agricultural productivity were assessed in the TD-treated samples and compared with untreated samples. Soil organic carbon decreased more than 25% in both the TD-treated topsoil and the subsoil, and total aggregation decreased by 20% in the topsoil but was unaffected in the subsoil. The alteration in these physical characteristics explains a 400% increase in saturated hydraulic conductivity in treated samples as well as a decrease in water retention at both field capacity and permanent wilting point. The changes in soil properties identified in this study suggest that TD-treated soils may still be suitable for sustaining vegetation, although likely at a slightly diminished capacity when directly compared with untreated soils.

Introduction

Crude oil and natural gas production within the Bakken and Three Forks shale formations has increased dramatically in the last decade and now contributes billions of dollars annually to economies in the northern Great Plains and southern Canada. However, accidental releases of petroleum products associated with this process can occur. In this region, which has been historically comprised of

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predominantly agriculture-based economies, these products are likely to be released in cropland and rangelands. These releases may be devastating both environmentally and economically, since the petroleum hydrocarbons (PHCs) from the oil can be directly toxic to vegetation, reduce plant germination and growth (Liste and Prutz, 2006; Kisic et al., 2009), change hydrology (de Jong, 1980; Roy and McGill, 1998), and inhibit biological activity in the soil (Dorn et al., 1998; Eom et al., 2007). These effects must be alleviated before the land can be returned to agricultural use. Thus, remediation methods in agronomic systems should be judged not only by the length of cleanup time and the ability to reduce PHC concentrations, but they must also demonstrate that remediated soil is capable of sustaining vegetation.

Ex situ thermal desorption (TD; Figure 4) is a remediation technique that can reliably meet cleanup standards in a shorter timeframe than many other strategies (Khan et al., 2004). Use of TD is effective in the removal of PHC contamination from a variety of causes, including coking plants (Biache et al., 2008), diesel fuel (Falciglia et al., 2011), and industrial waste (Norris et al., 1999). The TD process involves the excavation and thermal treatment of contaminated materials in a desorption unit that enhances contaminant vaporization (Lighty et al., 1990; US-EPA, 1994). The vaporized contaminants are passed through a thermal oxidation combustion chamber and released into the atmosphere, while treated soil is available for reuse.

Since most studies involving TD assess only contaminant removal (Falciglia et al., 2011; Tatano et al., 2013; Qi et al., 2014; McAlexander et al., 2015) and omit characterizing the soil, little information about the properties of TD treated soil exists. In the few studies that did assess some soil physical properties, TD altered particle size distribution (Bonnard et al., 2010) and reduced soil organic matter (SOM) (Tatano et al., 2013; Sierra et al., 2015). Additionally, TD treated soils used in greenhouse studies resulted in reduced plant growth (Dazy et al., 2009) and decreased activity in microorganisms (Cebron et al., 2011). Soil-water relationships in TD treated soil have not yet been described in the literature.

An additional, although not primary, function of TD is the creation of biochar when oxygen limiting conditions occur within the primary drum desorber (Tucker and Platts, personal communication, 2013). In some cases, biochar applications have been shown to increase surface area (Laird et al. 2010), soil organic carbon (SOC) (Sun et al., 2013), and water retention (Streubel et al., 2011; Ulyett et al., 2014). However, the quantification and characterization of biochar created from pyrolysis of SOM during the TD process has not been studied. Additionally, variability in the literature regarding the characteristics and effects on soil processes of biochar amendment demonstrates the uncertainty regarding effects of any biochar created during the TD process (Atkinson et al., 2010; Jeffery et al., 2011).

Though no opportunity exists to describe field-scale plant response in TD treated soils, assessing some physical and hydraulic properties of TD treated soils may indicate their potential for crop production. Increases in SOC (Monreal et al., 1997; Arvidsson, 1998), and aggregate stability (Barzegar et al., 2002) are both associated with higher crop yields. Additionally, crop production has been directly correlated with soil water retention (Martin et al., 2005), and numerous studies associate crop yields with hydraulic characteristics (O'Leary and Connor, 1997; Fernandez-Ugalde et al., 2009; Keller et al., 2012).

The purpose of this study was to evaluate how TD treatment affects the capacity of an agricultural soil to sustain vegetation. This evaluation was based on the examination of soil physical and hydraulic properties that have been associated with cropland and rangeland production. The results of this study may highlight benefits and drawbacks of using TD following contamination of agricultural soil and therefore influence future remediation projects.

Materials and Methods

Soil sampling

The soil samples were taken near an active remediation site in Mountrail County, North Dakota, USA (48°31'35.48"N, 102°51'25.72"W) that had been contaminated with Bakken crude oil as a result of a pipeline leak. The native, non-contaminated topsoil and subsoil used in this study were collected immediately outside the boundary of the remediation site. The soils are mapped as Williams-Zahl loams (Williams: Fine-loamy, mixed, superactive, frigid Typic Argiustoll; Zahl: Fine-loamy, mixed, superactive, frigid Typic Calciustoll), which have a productivity index of 76 and are considered "farmland of statewide importance" (NRCS-USDA, 2015).

Soil preparation

Native, non-contaminated topsoil (TS) and subsoil (SS) were treated separately, 2.9 Mg each, by a RS40 Thermal Desorption/Oxidation unit (TDU; Nelson Environmental Ltd., Edmonton, Alberta) at 350 °C for 15 minutes to generate TD treated topsoil (TS-TD) and TD treated subsoil (SS-TD). The four samples were air-dried, ground to pass through a 2 mm sieve, and stored at 20 °C in plastic containers. Subsamples used for aggregate stability testing were ground to pass through an 8 mm sieve.

Physical characteristics

Particle size analysis was conducted using the hydrometer method (Gee and Or, 2002; ASTM, 2007). Mineralogical analysis was performed using X-ray diffraction for quantitative analysis at a private laboratory (Activation Laboratories Ltd., Ancaster, Ontario, Canada). Total carbon (TC) and soil inorganic carbon (IC) were evaluated using a Primacs^{SLC} TOC Analyser (Skalar Analytical B.V., Breda, The Netherlands); soil organic carbon (SOC) was determined as the difference between TC and IC.

Specific surface area (SSA) was calculated using the ethylene glycol monoethyl ether (EGME) retention method (Pennell, 2002). Following the application of 2 mL of EGME to 1 g of oven-dry soil, samples were placed in a vacuum desiccator with anhydrous $CaCl_2$ and evacuated for 1 h. After 24 h, the samples were removed and weighed twice per day. The desiccator was evacuated following each weighing. When the weight of each sample was constant within ± 2.5%, SSA was calculated using the EGME conversion factor (Pennell, 2002).

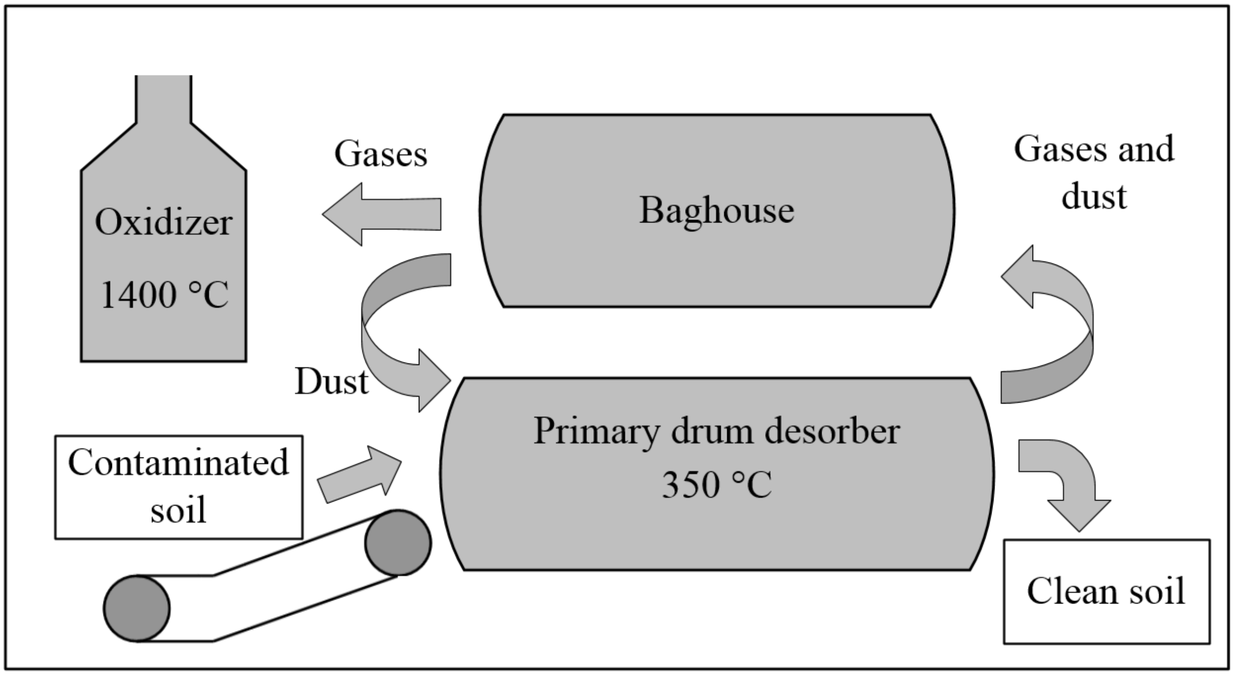

Figure 4. Schematic of thermal desorption process.

Aggregate stability and size distribution were calculated using the wet sieving method described by Six et al. (1998). Water stable aggregates were separated by wet sieving into three fractions: 1) microaggregates, between 53 and 250 µm; 2) small macroaggregates, between 250 and 2000 µm; and 3) large macroaggregates, between 2000 and 8000 µm. Aggregate samples were corrected for sand content according to Denef et al. (2001). Total aggregation was determined from the sum of micro-, small macro-, and large macro-aggregates. Four replications were completed for each of the physical parameters assessed.

Hydraulic characteristics

The water drop penetration time (WDPT) test was performed on 50 g of air-dried soil. Samples were placed in a petri dish, manually smoothed, and 6 50-µl drops of deionized water were placed systematically on the soil surface from a height of 1 cm (Hallin et al., 2013). The time for the drop to completely infiltrate the soil surface was recorded.

Saturated hydraulic conductivity (K_s) was determined using a constant head method with Tempe pressure cells (adapted from Reynolds and Elrick, 2002). Samples were placed into brass rings and impacted approximately 50 times to achieve bulk densities within ± 2.5% of one another. Samples were packed into Tempe cells and saturated from the bottom up with deaerated 0.01 M CaCl solution for 72 h. Once fully saturated, the liquid supply was attached to the top of each Tempe cell. Liquid passing through each cell was collected in beakers and measured every 30 min for at least 2 h. K_s was calculated using Darcy's law (Reynolds and Elrick, 2002). Leachate accumulated from the first 30 min of saturation from each cell was tested for dissolved organic carbon (DOC) using combustion catalytic oxidation with a TOC-V$_{CPH}$ Analyzer (Shimadzu Corporation, Kyoto, Japan).

Plant available water (PAW) and water retention values were determined using pressure plate extractors (Soilmoisture Equipment Corp., Goleta, CA) calibrated to five different pressures, 10, 33, 100, 500, and 1500 kPa. Rubber rings, 1 cm height and 5.5 cm diameter, holding approximately 25 g of soil were wetted with reverse-osmosis filtered water, placed on the pressure plates, and allowed to saturate for 4 h. Once saturated, each pressure was applied for 72 h, after which the gravimetric water content was determined. PAW was calculated by subtracting the volumetric water content at 1500 kPa from the volumetric water content at 33 kPa. Four replications were performed for each hydraulic characteristic assessed.

Statistical analysis

Results from the physical and hydraulic tests were analyzed using one-way analysis of variance (ANOVA) with mean difference significance at the $\alpha = 0.05$ level. Pairwise comparisons of all four samples were conducted with a post-hoc Tukey HSD test. All statistical tests were performed with R 3.2.1 software using the *stats* (R Core Team, 2014) and *multcomp* (Hothorn et al., 2008) packages.

Results and Discussion

Particle size distribution was not significantly affected by TD treatment; however, TD treatment in this study tended to cause a slight increase in sand-sized particles and a slight decrease in clay-sized particles in both the TS-TD and SS-TD (Table 2). These trends in particle size distribution were in accordance with other studies using TD, even those heated up to 500 °C (Bonnard et al., 2010) and 650 °C (Ourvard et al., 2011), which were temperatures substantially higher than achieved in this study. Similar decreases in clay-sized particles and increases in sand-sized particles as those in this study have been found in laboratory heating studies between 170 °C and 460 °C (Giovannini et al., 1988). Dramatic textural shifts can occur after heating at much higher temperatures (Zihms et al., 2013; Pape et al., 2015), because temperature thresholds at which clay minerals begin to deteriorate are normally above 500 °C (Tan et al., 1986). For example, the structure of bentonite, often composed of smectite minerals, does not deteriorate due to heating until temperatures reach over 700 °C; kaolinite structure begins to degrade at 530 °C (Tan et al., 1986). In this study, mineralogical analysis of TD treated samples indicate that deterioration of clay minerals did not occur (Table 3); as a result, the texture was not significantly changed. Nonetheless, the slight decrease in clay sized particles was the primary driver for a substantial reduction in SSA in this study, since clay sized particles generally dictate SSA (Petersen et al., 1996). Following TD treatment, SSA decreased by 20% in the TS-TD and 15% in the SS-TD samples (Table 2). Response of SOC shows a similar trend to SSA; TD treatment caused a 30% reduction in SOC in the TS-TD and 25% in the SS-TDU relative to untreated soil (Figure 5). This loss is roughly the same magnitude of other TD studies (Bonnard et al., 2010; Huang et al., 2011; Ourvard et al., 2011) and is expected when soils are heated to 350 °C (Varela et al., 2010; Kiersch et al., 2012), although that loss may be dependent on heating time. For example, shorter exposure to heating at 350 °C, only 10 min, could reduce the loss of SOC to approximately 12% (Thomaz and Fachin, 2014). Conversely, lengthening the heating time up to an hour could result in almost complete removal of SOC (Terefe et al., 2008; Zavala et al. 2010; Sierra et al., 2015). A major concern from an agronomic viewpoint is the mobility of the remaining SOC. After just 30 min of water flow under saturated conditions, the TS-TD horizon lost almost 0.1% of the DOC (Figure 6). Loss of DOC via leaching may have widespread implications on nutrient cycling and transport (Bolan et al., 2011); consequently, stabilizing the SOC should be considered when considering using these soils for agricultural production.

Table 2. Particle size distribution, specific surface area (SSA), and water drop penetration test (WDPT) time of untreated topsoil (TS) and subsoil (SS) and TD treated topsoil (TS-TD) and subsoil (SS-TD). Different letters within rows indicate significance at α=0.05 level in Tukey's HSD test.

	TS	TS-TD	SS	SS-TD
	Particle size distribution (% by weight)			
Sand †	47.3 ± 0.6	49.4 ± 1.4	48.0 ± 0.1	49.0 ± 1.0
Silt †	33.5 ± 0.8	31.9 ± 1.1	31.4 ± 0.8	32.2 ± 1.5
Clay †	19.2 ± 0.8	18.8 ± 0.3	20.6 ± 0.7	18.8 ± 1.2
	SSA ($m^2\ g^{-1}$)			
	89.6 ± 2.3ab	71.2 ± 4.3c	93.3 ± 3.4a	80.0 ± 4.2bc
	WDPT (s)			
†	< 1	1.16 ± 0.2	< 1	1.16 ± 0.2

† Indicates no significant differences at α=0.05 level within row

Table 3. Mineralogical analysis and distribution of clay fraction of untreated topsoil (TS) and subsoil (SS) and TD treated topsoil (TS-TD) and subsoil (SS-TD).

Mineral (% by weight)	TS	TS-TD	SS	SS-TD
Quartz	48.2	42.3	38.6	40.9
Plagioclase	17.4	16.8	13.9	13.6
Microcline	6.7	3.3	5.2	4.8
Muscovite/Illite	6.2	6	5.6	6.9
Kaolinite	0.6	0.7	0.7	trace
Amphibole	trace	trace	0.7	trace
Dolomite	2.1	2.9	4	2.5
Calcite	trace	0.4	1	1.1
Amorphous	18.9	27.5	30.2	30.1
Clay fraction (% by weight)				
Smectite	42	42	57	51
Illite	46	47	33	37
Kaolinite	8	8	7	9
Chlorite	4	3	3	3

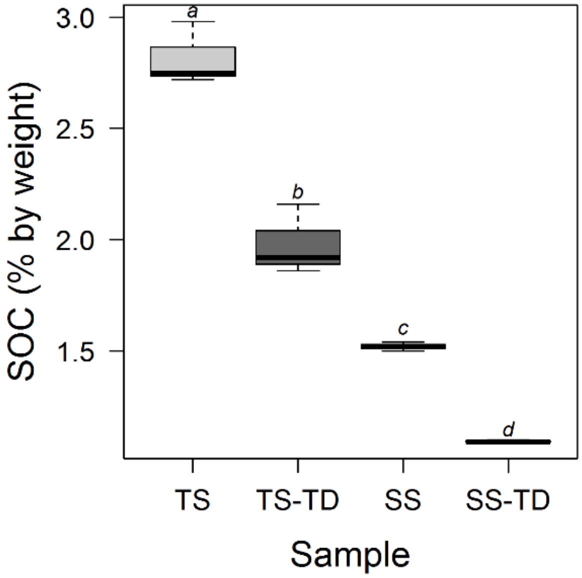

Figure 5. Boxplot of soil organic carbon (SOC) by weight of untreated topsoil (TS) and subsoil (SS) and TD treated topsoil (TS-TD) and subsoil (SS-TD). Different letters indicate significance at α=0.05 in Tukey's HSD test.

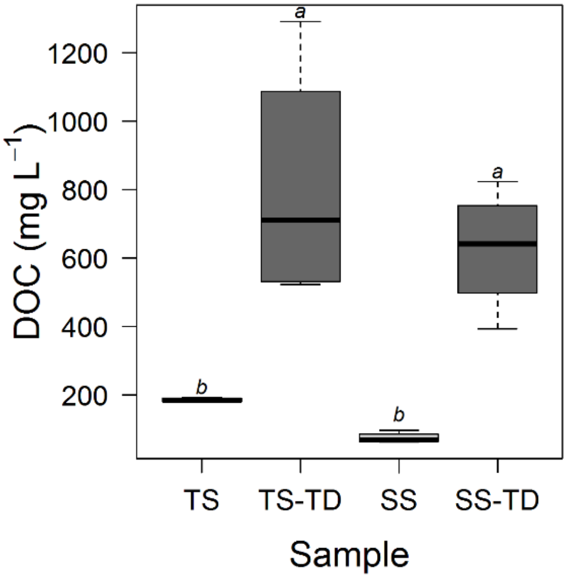

Figure 6. Boxplot of dissolved organic carbon (DOC) leachate taken from first 30 min of K_s test of untreated topsoil (TS) and subsoil (SS) and TD treated topsoil (TS-TD) and subsoil (SS-TD). Different letters indicate significance at α=0.05 in Tukey's HSD test.

The loss of SOC following TD treatment is likely linked to the reduction in total aggregation (Table 4), as many studies have noted the correlation between SOM or SOC and aggregate stability (Chaney and Swift, 1984; Jastrow, 1996; Six et al., 1998). However, these dynamics are complex during soil heating events (Mataix-Solera et al., 2011). Soils heated at lower temperatures (170 °C – 220 °C) may contain more water stable aggregates, likely due to hydrophobicity induced by heating (Garcia-Corona et al., 2004). Similarly, heating at much higher temperatures (750 °C – 1000 °C) can result in the re-aggregation of degraded minerals that may also exhibit greater aggregate stability (Campo et al., 2014). In this study, total aggregation was reduced by 20% in the TS-TD, which agrees with studies that describe a decrease in aggregate stability at temperatures between 350 °C and 400 °C (Varela et al., 2010; Zavala et al., 2010). Water stable aggregation did not decrease in the SS-TD, which agreed with other research that has found aggregate stability is not affected by loss of SOC associated with heating (Giovannini et al., 1988).

Table 4. Proportion of water stable aggregates within each size distribution. LM: 2000 – 8000 µm; SM:250 – 2000 µm; m: 53 – 250 µm; Total Aggregation 53 -8000 µm. Different letters within columns indicate significance at α=0.05 level in Tukey's HSD test.

	LM	SM	m	Total Aggregation
	g sand free aggregate g^{-1} soil			
TS	0.05 ± 0.007a	0.18 ± 0.004a	0.27 ± 0.013a	0.50 ± 0.012a
TS-TD	0.05 ± 0.008a	0.15 ± 0.006b	0.21 ± 0.007b	0.41 ± 0.010b
SS	0.01 ± 0.006b	0.12 ± 0.008c	0.29 ± 0.005a	0.41 ± 0.004b
SS-TD	0.04 ± 0.004a	0.11 ± 0.003c	0.24 ± 0.006b	0.39 ± 0.008b

While both of these responses have justification in the literature, differences in aggregation in the TS and SS is notable. Nearly every other metric assessed in this study found no difference between the TS-TD and SS-TD. Total aggregation may be an exception because it is so closely related to SOC, which was significantly different between the untreated TS and SS. The clay mineralogy may also be contributing to this behavior, as the higher SSA associated with the greater proportion of smectite in the SS may be more resistant disaggregation.

These changes in aggregation may affect hydraulic properties, such as infiltration. Increasing soil aggregation increases cumulative infiltration rates (Martens and Frankenberger, 1992), and infiltration rates decrease as the proportion of small aggregates increase (Loch and Foley, 1994). These decreases may be associated with an increased rate of surface seal deposition from the breakdown of smaller, weaker aggregates (Fox and Le Bissonnais, 1998). Thus, the combination of decreased SOC and a reduction in total aggregation may make TD treated soils especially susceptible to low infiltration rates and subsequent erosion (Lado et al., 2004). However, this occurrence may only be documented once the soils have been replaced and exposed to field conditions.

Similarly, initial infiltration rates could be inhibited by hydrophobicity that has been associated with soil heating (Garcia-Corona et al., 2004; Varela et al., 2010). However, the WDPT (Table 2) indicated that hydrophobicity is not evident following TD treatment, likely because the soils in this study were heated to 350 °C. Heat-induced hydrophobicity is generally highest when soils are heated between 175 °C – 200 °C (DeBano, 2000), but it decreases as heating temperature increases due to the loss of organic compounds (DeBano et al., 1976; Doerr et al., 2005).

In addition to influencing infiltration and erosion, texture, aggregation, and SOC all influence water movement within the soil (Olness and Archer, 2005; Dexter et al., 2008; Resurreccion et al., 2011; Arthur et al., 2012). Two good indicators of water movement are K_s and water retention. Relating to a texture gradient, K_s has an inverse relationship with the presence of clay sized particles while water retention has a positive relationship (Saxton and Rawls, 2006; Pachepsky and Park, 2015). While the texture of TD treated soils did not change significantly, the changes in K_s and water retention were more dramatic. Both the TS-TD and SS-TD K_s values were above 2.0 cm h^{-1}, which is a 400% increase from the TS and SS (Figure 7). Also, this K_s value of 2.0 cm h^{-1} is more characteristic of a sandy loam than a loam (Rawls et al., 1982). Similarly, the gravimetric water content at field capacity (33 kPa) and wilting point (1500 kPa) of the TD treated samples were 19% and 9%, respectively (Table 5), which were more comparable with a sandy loam rather than a loam (Saxton and Rawls, 2006). Thus, some of the hydraulic characteristics of the TD treated soils seem to belie the properties normally associated with its texture.

Looking beyond texture, these discrepancies may also be explained by the interaction of SOC and aggregation. Decreases in SOC and aggregation can reduce water retention (Rawls et al., 2003) and PAW (Olness and Archer, 2005). Interestingly, PAW did not follow the trends shown in the K_s and water retention. Although gravimetric water content decreased with increasing pressure (Table 5), the rate of decrease was similar between untreated and TD treated samples. Therefore, PAW remained relatively constant following TD treatment, and the values were all fairly representative of other loams (Cassel and Sweeney, 1974). Although this study did not attempt to quantify the biochar created during the TD process, it is likely that some form was present. Regardless, the type and amount created was not sufficient to keep physical and hydraulic parameters consistent with untreated soil.

Table 5. Gravimetric soil water content with standard error at various pressures (bars) for untreated topsoil (TS) and subsoil (SS) and TD treated topsoil (TS-TD) and subsoil (SS-TD). Different letters within columns indicate significance at α=0.05 level in Tukey's HSD test.

	Soil moisture pressure (kPa)					Plant available water
	10	33	100	500	1500	
	Gravimetric water content (% by weight)					$cm^3\ cm^{-3}$
TS	26.1 ± 1.19[†]	22.9 ± 0.35a	20.1 ± 0.3a	13.2 ± 0.03a	12.2 ± 0.03a	11.3 ± 0.37[†]
TS-TD	23.3 ± 1.07	18.6 ± 0.2b	16.1 ± 0.15b	10.7 ± 0.22c	8.94 ± 0.05c	10.1 ± 0.25
SS	25.7 ± 1.3	21.6 ± 0.37a	19.7 ± 0.2a	12.2 ± 0.13b	10.6 ± 0.1b	11.5 ± 0.41
SS-TD	22.8 ± 0.57	19.7 ± 0.4b	16.0 ± 0.36b	10.8 ± 0.14c	8.74 ± 0.06c	11.5 ± 0.46

[†] Indicates no significant differences at α=0.05 level within column

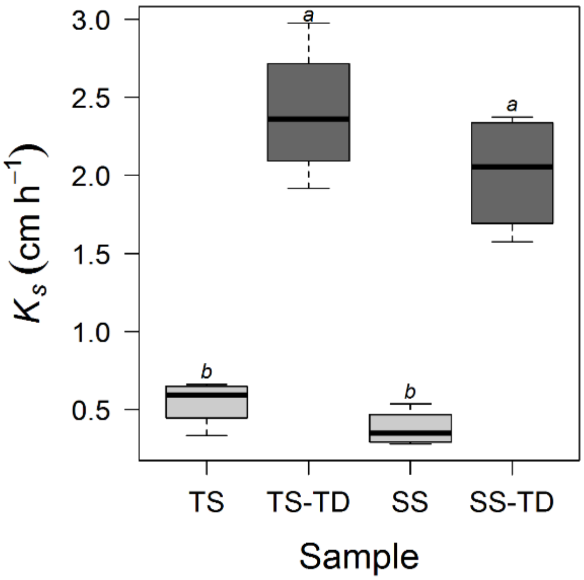

Figure 7. Boxplot of saturated hydraulic conductivity (K_s) of untreated topsoil (TS) and subsoil (SS) and TD treated topsoil (TS-TD) and subsoil (SS-TD). Different letters indicate significance at α=0.05 in Tukey's HSD test.

The information obtained from these physical and hydraulic parameters can begin to answer two vital questions about using TD treated soils to remediate soil in agricultural regions. First, will agricultural productivity of a certain soil change following TD treatment? The results of this study suggest that a decrease in yield is possible when comparing TD treated soils to pre-treated levels. Although texture was not significantly altered by TD treatment, the K_s and water retention of TD treated samples responded as though the distribution of sand sized particles had increased substantially. This behavior may indicate reduced yield potential, since soils with more sand sized particles have been associated with lower yields than soil with more fine particles (Simpson and Siddique, 1993; Nyiraneza et al., 2012), mostly due to soil-water relationships. Further, the loss of SOC, accompanied by decreased aggregation in the TD treated soils, could result in increased compaction (Baumgartl and Horn, 1991) and associated reduced yields (Oussible et al., 1992; Gregorich et al., 2011). This loss of SOC could be exacerbated through additional leaching due to an increase in K_s.

The second question this study can address is much broader: can TD treated soil be used for agricultural production? While direct comparison between pre-treatment and post-treatment soils indicates that TD treatment alters some soil characteristics, the extent of these alterations do not appear significant enough to prevent use for crop production. Even though the TD treated soil behaves more like a sandy loam than its measured texture, sandy loams are routinely used in crop systems. Additionally, the characteristics identified to change with TD treatment could all be modified with soil amendments; applying organic amendments would increase the SOC and likely increase aggregation and water retention, as well as slow DOC leaching by reducing K_s.

Conclusions

These laboratory assessments of TD treated soils suggest that water balances, dictated by SSA, SOC, and aggregation, are the primary area of concern when considering using TD for remediation in agricultural systems. The changes to these physical and hydraulic properties revealed in this study indicate that returning TD treated soil to pre-treatment levels of productivity may require additional management, likely soil amendments such as manure or compost. Additionally, to more fully answer these questions about the suitability of TD treated soils for use as topsoil in agricultural systems, the effects of TD treatment on soil chemical and biological parameters should also be investigated. A notable distinction to this study is that it used non-contaminated samples. Incorporating varying levels of pollutants, especially crude oil, into the soil before TD treatment may have distinctly different effects on the characteristics studied here. However, this study offers valuable baseline knowledge regarding what the TD process does to non-contaminated soils so that comparisons may be made in the future using contaminated soils.

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CHAPTER 3. WHEAT GROWTH IN SOILS TREATED BY EX SITU THERMAL DESORPTION[2]

Abstract

Successful remediation of oil-contaminated agricultural land may include the goal of returning the land to pre-spill levels of agricultural productivity. This productivity may be measured by crop yield, quality, and safety, all of which are influenced by soil characteristics. This research was conducted to determine if these metrics are affected in hard red spring wheat (*Triticum aestivum* L. cultivar: Barlow) when grown in soils treated by *ex situ* thermal desorption (TD) compared to wheat grown in native topsoil (TS). Additionally, TD soils were mixed with TS at various ratios to assess the effectiveness of soil mixing as a procedure for enhancing productivity. In two greenhouse studies, TD soils produced similar amounts of grain and biomass as TS, although grain protein in TD soils was 22% (± 7%) lower. After mixing TS into TD soils, the mean biomass and grain yield were reduced by up to 60%, but grain protein increased. These trends are likely the result of nutrient availability determined by soil organic matter and nutrient cycling performed by soil microorganisms. TD soil had 84% (± 2%) lower soil organic carbon, and cumulative respiration was greatly reduced (66% ± 2%). From a food safety perspective, grain from TD soils did not show increased uptake of polycyclic aromatic hydrocarbons. Overall, this research suggests that TD soils are capable of producing safe, high quality grain yields in controlled environments.

Introduction

Accidental releases during the extraction, transport, and storage of crude oil can expose soil to high levels of petroleum hydrocarbons (PHCs). These PHCs harm soil health (Eom et al., 2007; Roy and McGill, 1998), reduce seed germination (Yi et al., 2016; Tang et al., 2011), and hinder vegetative growth (Essien and John, 2010; de Jong, 1980). When these releases occur on agricultural land, soil remediation is required to return the land to pre-contaminated levels of productivity. While pre-contaminated levels of productivity may not be immediately feasible in some cases, restoring productivity is a long-term goal at many contaminated sites. Many techniques exist to remediate PHC contamination

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in soil (Lim et al., 2016), and the most appropriate technology to implement is dictated by site-specific considerations.

One established technique that may be suitable for remediating agricultural soil is *ex situ* thermal desorption (TD), which can be widely applied due to its versatility, relatively short treatment time, and the ability to reuse the treated soil (de Percin, 1995). Briefly, TD enhances contaminant vaporization by heating contaminated materials in a desorption unit (USEPA, 1994; Lighty et al., 1990). The vaporized contaminants are combusted in a thermal oxidation chamber, and the treated soil is rehydrated and available for reuse. This technique has been used to treat a variety of contaminants (Sierra et al., 2016; Qi et al., 2014; Falciglia et al., 2011), as the heating temperature and heating time can be manipulated to target volatile and semi-volatile compounds in a variety of soil matrices.

An appealing aspect of using TD to remediate contaminated agricultural soil is the possibility of soil reuse following treatment, although the capacity of TD soils to sustain vegetation has not been fully explored. Numerous studies have shown that TD soils are capable of producing more biomass than contaminated, untreated soils (Ourvard et al., 2011; Wang et al., 2010; Dazy et al., 2009; Roh et al., 2000); however, these studies offer no comparison with non-contaminated soils. Thus, they do quantify the differences between remediated soil and non-contaminated soil, which is essential to gauge progress toward attaining pre-spill productivity.

In two studies that did offer direct comparison between TD soils and non-contaminated soils, seed germination, shoot growth, and biomass were between 40% and 80% lower in TD soils (Yi et al., 2016; Vidonish et al., 2015). Notably, these plants did not grow to maturity, so TD effects on later life stages of the plant is unknown. Additionally, the effects of TD on plant growth may vary among species (Yi et al., 2016; Dazy et al., 2009), so translating this information to common agricultural crops requires species-specific research. Further, none of these studies involving TD soils quantified post-TD contaminant uptake into plant structures. Since TD may only be applied to attain regulatory standards, PHC concentrations may remain above background levels. Thus, food safety must also be a consideration when assessing the viability of using TD soils for agricultural production.

While biomass and quality of vegetation may be valuable indicators for meeting remediation goals, these factors alone do not encompass a holistic approach to soil remediation. Plant response is closely tied to the alteration of soil properties following TD that are, in turn, linked with long-term processes vital in maintaining soil health. Notable changes in soil properties following TD are reduced soil organic matter (SOM) (Sierra et al., 2016; Yi et al., 2016; McAlexander, 2015) and increased pH (Yi et al., 2016; Ourvard et al., 2011), although the magnitude of these alterations are dependent on heating temperature, time, and native soil properties. Soil physical properties also change following TD treatment at 350 °C, including a reduction of total aggregation, a sharp increase in saturated hydraulic conductivity (O'Brien et al., 2016), and decreased water retention (Roh et al., 2000). Further, when comparing TD soils to non-contaminated soils, biological communities are altered (Cebron et al., 2011), microbial abundance is decreased (Yi et al., 2016; Ourvard et al., 2011), and genotoxicity to earthworms is increased (Bonnard et al., 2010). Projects aimed at returning the land to pre-contaminated conditions need to account for these changes, as each of these properties relates to short-term plant production, as well as long-term soil health.

One possible way to mitigate these effects of TD may be to mix native, non-contaminated topsoil with TD soil. Incorporating the native topsoil increases SOM and can rapidly reintroduce a native biological community (Marschner and Rumberger, 2004), both of which benefit long-term soil health. In some circumstances, soil mixing may be an alternative to purchasing replacement topsoil, a common practice in remediation projects. Introducing topsoil from another location may be undesirable due to unknown soil management history and possibility of weed species in the seedbank or plant pathogens. Therefore, the practice of soil mixing may both reduce overall project costs and improve soil quality.

The purpose of this research was to assess the potential of TD soils in cropland production, both as a singular product and as a mixing agent with non-contaminated topsoil. This assessment was based on two greenhouse studies conducted using TD soil to grow hard red spring wheat (HRSW). Both studies, referred to as “Study 1” and “Study 2,” included measurements of biomass production, grain yield, and grain quality. Study 1 also evaluated the accumulation of polycyclic aromatic hydrocarbons (PAHs) in grain, while Study 2 contextualized the trends in wheat growth with measurements of soil respiration and C:N dynamics. This research is valuable because it provides direct comparison between TD soils and native, non-contaminated soils using a commonly grown commodity crop. Thus, the findings of this study are relevant in planning future remediation projects involving agricultural soil aimed towards returning the land crop production.

Materials and Methods

Soil source, properties, and preparation

The two studies were conducted in a greenhouse at North Dakota State University, Fargo, ND. The treatments for each experiment were a series of mixtures comprised of two different soil materials: 1) TS: native, non-contaminated topsoil taken from 0-20 cm depth, and 2) TD: PHC-contaminated soil that had been treated by *ex situ* thermal desorption. In Study 1, treatments were comprised, by weight, of 100% (TD), 90% (TD90), 70% (TD70), 40% (TD40), and 0% (TS), respectively, of TD soils. In Study 2, treatments were comprised of 100% (TD), 95% (TD95), 75% (TD75), 50% (TD50), and 0% (TS), respectively, of TD soils; the balance of weight in each treatment was filled by TS. Notably, the TD soil material was a mixture of contaminated subsoil from up to 15 m below ground surface, so it did not originate from the zone of soil genesis. Thus, it is not necessarily directly comparable to TS. Despite this distinction, for ease of reference, this material will be referred to hereafter as “TD soil”. This material was thoroughly mixed in a stockpile prior to treatment, so specific depth of TD soil in the profile could not be identified.

The TS was mapped as Williams-Zahl loam (Williams: Fine-loamy, mixed, superactive, frigid Typic Argiustoll; Zahl: Fine-loamy, mixed, superactive, frigid Typic Calciustoll) (NRCS 2015). The TD soils were contaminated *in situ* with Bakken crude oil from a pipeline leak before being excavated, mixed in a stockpile, and treated by a RS40 Thermal Desorption/Oxidation unit (Nelson Environmental Ltd., Edmonton, Alberta) at 350 °C for 10 min. Soil characteristics for the TS and TD soil are shown in Table 6. Finally, soils were passed through a 6 mm sieve, air-dried at 25 °C, and stored in plastic containers in a climate-controlled greenhouse prior to the study.

Experimental setup

In both Study 1 and Study 2, mixtures were created by adding the soil for each pot to a two shell dry blender (Patterson-Kelly, Co., East Stroudsburg, Pennsylvania) and mixing for 5 min. Each pot in Study 1 (40 total) held 4 kg of soil, while those in Study 2 (40 total) held 3 kg of soil. Plastic bags were placed within the pots to prevent leaching of water. Both studies received the same fertilizer treatments.

Soil P was normalized by adding dissolved calcium monophosphate ($Ca(H_2PO4)_2$) at varying levels per treatment to reach a target rate of 15 mg P kg^{-1} (Franzen, 2014). Each pot was then subjected to one of two N treatments: 1) no additional N, or 2) N addition to a target rate of 62.5 mg N kg^{-1} (Franzen, 2014). To attain the target N rate, dissolved calcium nitrate ($Ca(NO_3)_2$) was added at varying rates depending on starting concentration.

In Study 1, 18 HRSW (*Triticum aestivum* L. cultivar: Barlow) seeds were sown 2.5 cm deep into each pot using three rows of six seeds. Seeds were spaced 2 cm apart, rows spaced 4 cm apart, and pots were covered to retain moisture during the germination period. Fourteen days after sowing (DAS), the number of seeds per pot was reduced to six. In Study 2, 12 HRSW seeds were sown 2.5 cm deep into each pot in a circle around an open middle and covered during the germination period. At the time of seeding, a PVC ring (10 cm diameter, 3 cm high) was installed to 1.5 cm depth to accommodate soil respiration sampling described below. At 14 DAS, the number of seeds per pot was reduced to six. In both studies, pots were watered up to 80% of field capacity (volumetric water content at 33 kPa) every other day, and position in the greenhouse was rotated biweekly. Both studies were terminated after 12 weeks.

Data collection

Plant growth and soil nutrients

After termination, the aboveground biomass was clipped at 1 cm above the soil surface, dried at 60 °C, and weighed. Grain was dried at 60 °C, weighed, and a subsample was used to quantify N using the combustion method (Agvise Laboratories, Northwood, ND); a conversion factor of 5.6 (Tkachuk, 1969) was used to determine protein content. Soil cores were taken from the center of each pot to a depth of 14 cm using a 4 cm diameter hand probe, and subsamples from the cores were analyzed for parameters shown in Table 6. After removing the cores, the remaining soil in each pot was screened through a 2 mm sieve. Roots retained on the sieve were collected, washed, dried at 40 °C, and weighed. SOC was determined as the difference between total carbon and total inorganic carbon found using a Primacs TOC Analyzer (Skalar Analytical B.V.). pH and EC were both found using 1:1 soil-water extraction (Watson and Brown, 1998; Whitney, 1998a; Agvise Laboratories). Plant available NO_3-N and NH_4-N were determined using KCl extraction, and P was quantified by the Olsen method (Frank et al., 1998; Mulvaney, 1996; Agvise Laboratories). Plant available K, Ca, Mg, and Na were quantified by optical emission ICP (OE-ICP) using the ammonium acetate extraction method (Warncke and Brown, 1998; Agvise Laboratories). Fe and Mn were found with the DTPA Sorbitol method (Whitney, 1998b), and Cl was found with the Hg (II) thiocyanate method (Gelderman et al., 1998; Agvise Laboratories).

Table 6. Selected soil properties of native, non-contaminated topsoil (TS) and subsoil material treated by thermal desorption (TD) at time of planting. Standard error included in parentheses. TS and TD were the same materials in both Study 1 and Study 2. The values for the soil mixtures in both studies can be calculated using the TS:TD ratio of each treatment.

		Soil	
Soil property		TS	TD
Sand	*g kg⁻¹*	454 (23)	434 (17)
Silt	*g kg⁻¹*	330 (90)	326 (14)
Clay	*g kg⁻¹*	219 (22)	239 (9)
SOC	*g kg⁻¹*	30 (4)	1.5 (0.7)
EC	*dS m⁻¹*	0.3 (0.1)	1 (0.3)
pH		7.4 (0.2)	8.2 (0.1)
TPH	*mg kg⁻¹*	42 (13)	101 (63)
NO_3	*mg kg⁻¹*	17.6 (0.8)	0.7 (0.1)
NH_4	*mg kg⁻¹*	10.2 (0.9)	7.8 (0.2)
P	*mg kg⁻¹*	8.9 (0.2)	3.3 (0.2)
K	*mg kg⁻¹*	248 (2)	193 (1)
Ca	*mg kg⁻¹*	3216 (59)	4707 (17)
Mg	*mg kg⁻¹*	636 (8)	690 (5)
Na	*mg kg⁻¹*	17.4 (0.2)	114 (2)
Fe	*mg kg⁻¹*	49.1 (1.7)	10 (0.1)
Mn	*mg kg⁻¹*	51.1 (5.2)	25.4 (0.6)
Cl	*mg kg⁻¹*	1.9 (0.1)	20.1 (0.3)

EC: Electrical conductivity; SOC: Soil organic carbon; TPH: Total petroleum hydrocarbons

Study 1: Contaminant uptake

For Study 1, subsamples from cores of TD and TS were evaluated for TPH concentration within the C10-C36 range using EPA 8015 method modified with silica gel (Pace Analytical Services, Inc. St. Paul, MN). Additionally, grain samples were analyzed for the presence of 16 PAHs regulated by the EPA (Keith, 2015) using EPA 8270 by selected ion monitoring (Pace Analytical Services, Inc., Green Bay, WI). Due to analysis costs, each treatment within the N-added and no N-added blocks was pooled together for quantifying PAHs. Given the results from Study 1, as well as the high cost, the same analysis was not performed in Study 2.

Study 2: Root analysis and soil respiration

For Study 2, roots were collected off a 2 mm sieve and, prior to drying and weighing, scanned and analyzed using WinRhizo 2012 software (Regent Instruments, Inc., Quebec Ontario) to obtain root length, surface area, and volume (adapted from Bauhus and Messier, 1999). Soil respiration was quantified by weekly measurements of CO_2 efflux taken from each pot using an environmental gas monitor (EGM-4) equipped with a soil respiration chamber (Fouche et al., 2014; SRC-1; PP Systems, Amesbury, MA) that attached to the PVC ring installed in each pot. The order of data collection from the pots was systematically rotated each week to avoid bias based on sampling time of day.

Statistical analysis

Although the intent of using different ratios in Study 2 was to build a regression of soil mixtures by percentage, the variability inherent in greenhouse studies, as well as the differences in pots and amount of soil used, required that statistics be analyzed on each study separately. Biomass and yield parameters were reported relative to the mean of TS for each respective study to allow for better comparison between Study 1 and Study 2. The remaining measurements were left in absolute terms.

All biomass and grain results were analyzed using one-way analysis of variance (ANOVA) with mean difference significance at $\alpha = 0.05$. Pairwise comparisons were conducted with a post-hoc Tukey HSD test. All statistical tests were performed with R 3.2.1 software using the *stats* (R Core Team, 2014) and *multcomp* (Hothorn et al., 2008) packages.

Results and Discussion

Wheat growth

The trends in wheat biomass growth and grain yield were similar in both studies (Figure 8), although total biomass and grain production were much greater in Study 1 than Study 2 (data not shown). In addition to overall reduced growth, no response to N-addition was evident in Study 2; thus, analyses of data from Study 2 were not partitioned by N application. Nonetheless, the relative growth trends were similar between Study 1 and Study 2. The TD soils produced as much biomass as TS, except in the no N-added pots in Study 1. Creating soil mixtures by addition of TS to TD soils resulted in a severe decrease in biomass growth and grain yield, although these metrics recovered with a greater proportion of TS added to the mixtures. Wheat response was likely unaffected by TPH levels, since TPH levels of 1000 mg kg^{-1} and above have not inhibited wheat germination, root elongation (Shahsavari et al., 2013; Tang et al., 2011), biomass (Issoufi et al., 2006), or yield (Kisic et al., 2010).

In Study 1, TD soils without N-addition produced about 40% as much grain as TS, which corroborates with other studies where growth in TD soils was 40-60% that of uncontaminated soil (Yi et al., 2016; Vidonish et al., 2015). This response is likely the result of less plant available N and SOC in the TD soils than TS soils at time of planting (Table 6). These lower quantities of available nutrients may be the result of using subsoil material for the TD treatment and/or because plant available nutrient levels and SOM were altered by the soil heating process. Increasing the temperatures above 220 °C, as occurred in this study, results in losses of organic N through the destruction of SOM (Varela et al., 2010) and increased losses of plant available N (Pape et al., 2015); consequently, plant production is also reduced (Giovannini et al., 1990).

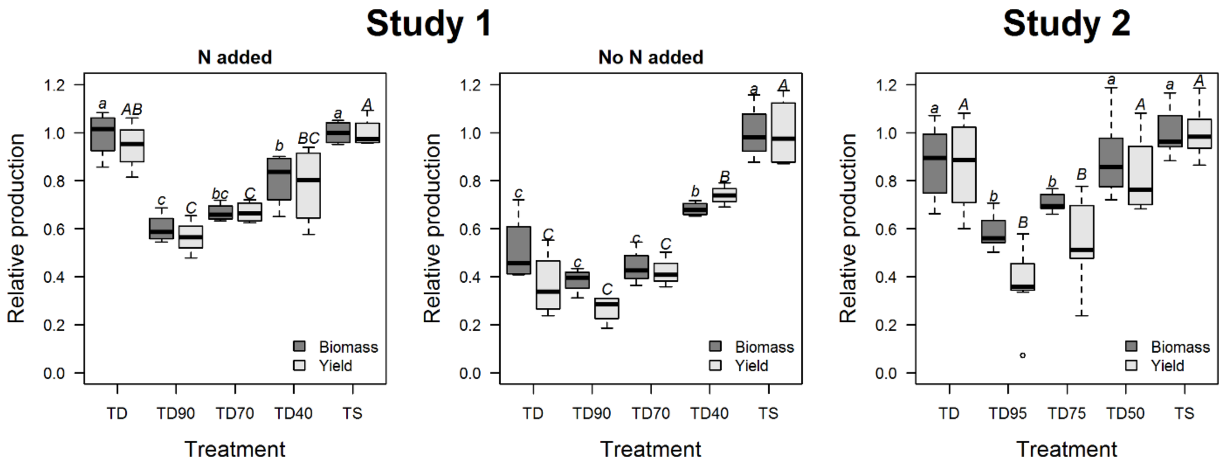

Figure 8. Boxplots showing relative wheat production of biomass and grain yield with respect to the mean value of TS for each plot, respectively. Different letters within boxplots indicate significance at α=0.05 level in Tukey's HSD test, with lower case letters corresponding to biomass and uppercase letters corresponding to grain yield. Study 1 is divided by pots with N-added (up to 62.5 mg N kg^{-1}) and no N-added. Study 2 had the same fertilizer application, but no statistical response to fertilizer was evident; thus, all pots from Study 2 are shown together.

The wheat growth in TD soils in the N-added pots from Study 1, as well as all TD soils in Study 2, was comparable to the TS (Figure 2). This production is likely the result of controlled growing conditions and abundance of soil nutrients and water, so these results may not be reproduced under field conditions. Notably, this research utilized plastic bags to prevent leaching through the duration of the experiment. Since TD treatment sharply increases soil saturated hydraulic conductivity (O'Brien et al., 2016) and decreases water retention (Roh et al., 2000), it may likely enhance the leaching of SOC when saturated (O'Brien et al., 2016), causing losses of plant available nutrients. Under field conditions, these losses would vary and be difficult to account for with fertilizer rates in non-irrigated environments. Nonetheless, this study showed that under appropriate nutrient management and no water stress, TD soils could match TS in wheat growth and productivity. Thus, mitigating the losses associated with altered water balances and decreased SOC may be a promising strategy for using TD soils in remediation projects.

While adding TS to TD soils may increase SOC and reduce leaching, this mixing was accompanied by a sharp decline in wheat production. In both studies, the addition of any TS to TD soils resulted in significant declines in biomass growth (up to 40%) and yield (up to 60%). This growth reduction following soil mixing agrees with findings of Roh et al. (2000), where fescue (*Festuca arundinacea*) grown in a 1:1 mixture of TS and TD soil produced half as much biomass as the TD soil alone. This growth trend is likely the result of biological interactions associated with the reintroduction of soil microorganisms into the TD soil and alterations of total soil N and total soil C pools; this interaction is explored more fully later.

Wheat quality

Grain protein content also showed a response to N-application in Study 1 but not in Study 2. In both studies, the TD soils produced grain with less protein than other treatments (Figure 9). While nearly all values reported in this study are higher than 152 g kg^{-1}, the typical protein content in field grown Barlow HRSW (Mergoum et al., 2011), the comparatively low values in TD soils indicate an underlying issue. In Study 1, this reduced protein content in the grain is likely due to N deficiency at the grain filling stage. Protein content in grain grown in TD soils was less than (unfertilized pots) or very close to (fertilized pots), a critical value of 130 g kg^{-1} for HRSW grown in the northern Great Plains (Selles and Zentner, 2001); protein content below these levels normally indicates that the wheat is N deficient at time of harvest.

While low protein indicates N deficiency, high protein does not necessarily indicate sufficient N levels (Selles and Zentner, 2001). Thus, the higher values in Study 2 may not imply that wheat in TD soils were not N deficient, especially given the comparatively low protein content. Rather, these lower

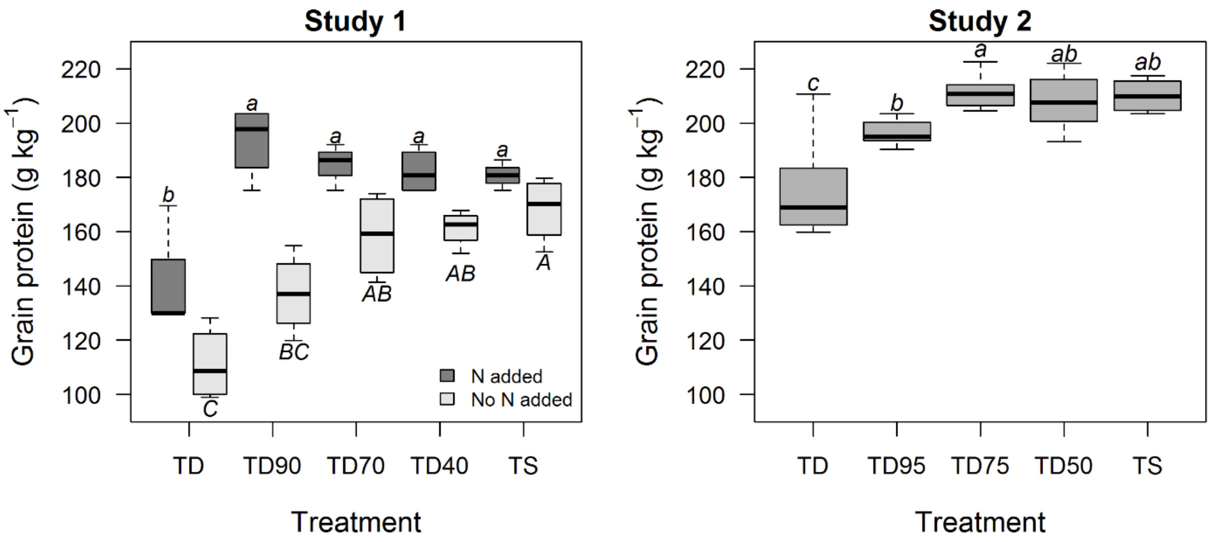

Figure 9. Protein content of wheat grown in Study 1 and Study 2. Study 1 is separated by pots with N-added (up to 62.5 mg N kg^{-1}) and no N-added. Different letters within boxplots indicate significance at α=0.05 level in Tukey's HSD test, with lower case letters corresponding to pots with N-added, and uppercase letters corresponding to pots with no N-added. Study 2 had the same fertilizer application, but no statistical response to fertilizer was evident; thus, all pots from Study 2 are shown together.

protein levels suggest that timing plays a role in the differences in N availability in TD soils, since biomass production was comparatively high. This timing indicates that the wheat grown in TD soils depleted the available N during biomass production, and the soil did not have sufficient buffer capacity or mineralization rate to replenish plant available N at the time of grain filling. Conversely, the TS and mixtures all have higher protein levels, which could indicate higher levels of available N at the grain filling stage (Beres et al., 2008). Therefore, these findings imply a mechanism associated with N cycling that differs between the TD-only pots and the pots containing some TS. This mechanism is likely biological and related to SOM, as soil physical and chemical characteristics are not drastically changed following TD treatment (O'Brien et al. 2016; Sierra et al., 2016; Roh et al., 2000). Consequently, Study 2 incorporated soil respiration and analysis of total C and total N pools to contextualize some of the biomass trends.

Soil respiration and C and N pools

Soil respiration may be used as an indicator for microbial abundance and activity associated with nutrient cycling (Luxhoi et al., 2006). However, these relationships may not be exact due to total respiration being the sum of several sources of CO_2 efflux (Kuzyakov, 2006), including soil fauna, root, and microbial respiration. In this study, no soil macrofauna were in the pots, and no aboveground plant structures were in the chamber during measurement, so plant respiration was limited to the root structures. Generally, as root biomass increases, respiration increases (Qiao et al., 2009; Kocyigit and Rice, 2006). However, no metrics of root growth varied significantly between treatments (data not shown), so differences in overall respiration in this study are likely not associated with root respiration but are based on microbial respiration.

The cumulative respiration was three times higher in TS than TD soils (Figure 10). Total respiration values determined for TS were similar to those found under a wheat system in a field experiment (Frank et al., 2006) and slightly lower than values found under winter-wheat soybean rotation in a field experiment (Hu et al., 2013). In comparison to these field experiments, the respiration under TD soils in this study was greatly diminished. Further, the reduction grew more severe over time, as the respiration rate decreased sharply in the final three weeks in both TD and TD95 pots, while the rates remained steady in TS, TD50, and TD75. Relative to TS, mean values for respiration during the first 9 weeks in TD and TD95 were 32% (± 4%) and 34% (± 5%), respectively. In the final 3 weeks, these mean values dropped to 17% (± 4%) for TD and 24% (± 5%) for TD95. This stagnation in respiration may represent a point in time in which resource stores from fertilization were depleted, so these values may be more indicative of respiration in TD soils without additional resource input.

This decreased respiration in TD soils may be explained by lower microbial biomass (Colman and Schimel, 2013) associated with lower SOC, especially as the soil mixtures showed increasing respiration as more TS was added. Addition of SOC to TD soils via TS mixing likely resulted in microbial recolonization (Marschner and Rumberger, 2004), since microbial biomass and activity are diminished in the TD process (Yi et al., 2016; Cebron et al., 2011). In other cases of recolonization of microbial communities following soil heating, the microbial reestablishment is normally accompanied by a burst of soil respiration (Barcenas-Moreno et al., 2014; Barcenas-Moreno and Baath, 2009). In this study, the burst would be expected following soil mixing due to the addition of SOC to the TD soils, as well as the fertilizer application.

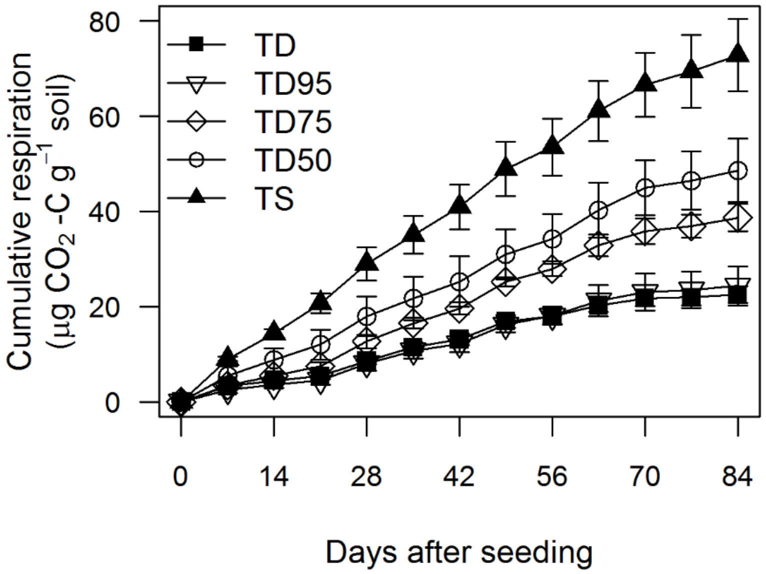

Figure 10. Mean cumulative respiration for each treatment throughout the course of Study 2. Each data point is the mean value of all pots within a given treatment for each week and is shown with standard error bars.

Notably, this study did not find an initial burst, as the magnitude of respiration did not change greatly between weeks until the final three weeks (Figure 10). This lack of response is likely because measurements were taken every seven days, so any response between measurements was not observed. The timeframe for this recolonization can be very short, as bacteria levels may recover and stabilize within 5 days (Barcenas-Moreno et al., 2011). Although this reestablishment and stabilization can occur rapidly (Barcenas-Moreno and Baath, 2009; Guerrero et al., 2005), microbial populations may require more than a year to reach background levels (Hamman et al., 2007). Further, these soils were heated up to 18 months before the mixing, so some level of stabilization following recolonization by wind deposition and dust particles may be expected prior to this study. Once stabilized, the long-term respiration trends and associated biological processes were likely regulated by soil N and C pools rather than the effects of the TD process.

Respiration was correlated with both total soil N and SOC (Figure 11, A and B). These figures identify clear group separation based on the treatments, with the exception of TD and TD95, which suggests that addition of only 5% TS may be insufficient for recovery of microbial communities in one

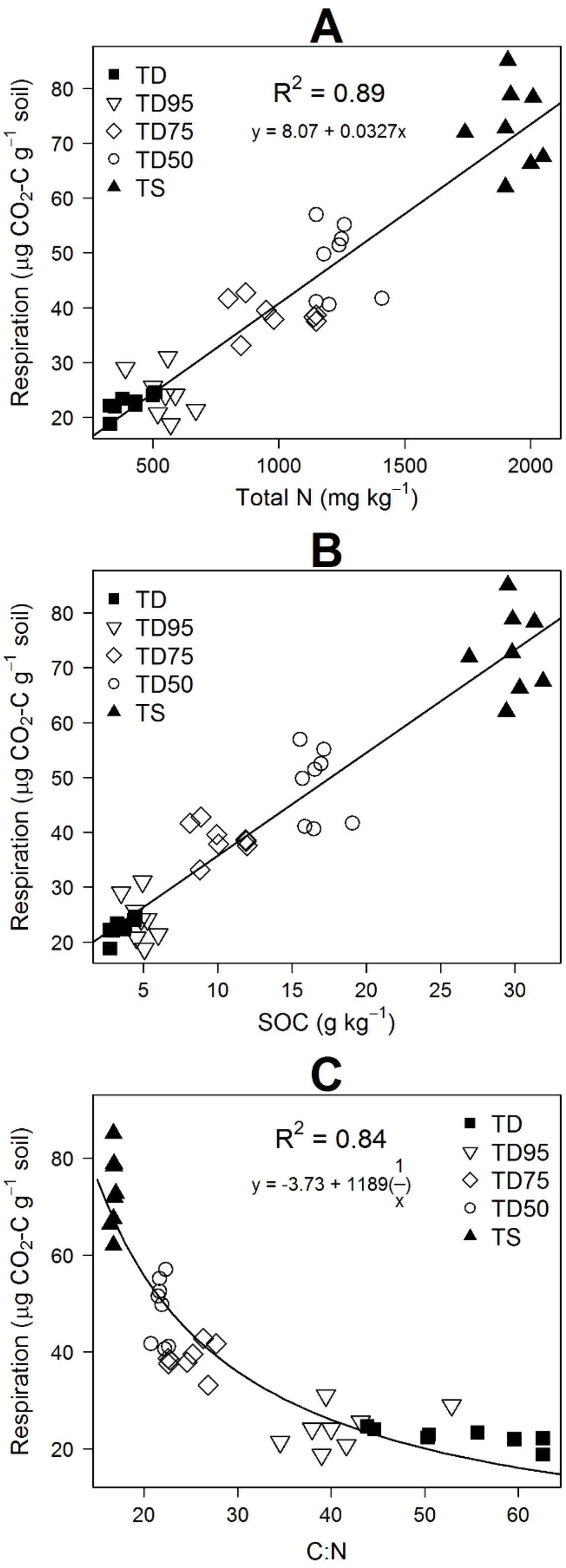

Figure 11. Cumulative respiration plotted with A) total soil N; B) total soil organic carbon (SOC); and C) soil C:N for each treatment in Study 2.

growing season. These respiration levels may also be used to make inferences about N cycling, as several studies have identified correlations between respiration and both gross immobilization and gross mineralization (Luxhoi et al., 2009; Bengtsson and Bergwall, 2006; Hart et al., 1994). Thus, much more immobilization and mineralization are likely occurring in the TS than the TD soil, and these metrics increase in TD soil as more TS is added.

Conversely, C:N ratios show an inverse correlation with respiration, but the group separation is still evident (Figure 11C). While respiration values may serve as good indicators of gross mineralization and immobilization, they are not good predictors of net mineralization and immobilization (Song et al., 2011; Hart et al., 1994), so the partitioning of those values is unclear. However, net N mineralization and immobilization may be correlated with C:N (Accoe et al., 2004; Barrett and Burke, 2000). Generally, the C:N ratios above 20 will result in net immobilization, whereas the lower ratios will result in net mineralization. This study identified values that indicate a close balance of mineralization and immobilization in the TS and TD50, whereas the remainder of the treatments tended towards net immobilization.

Despite reduced overall cycling and a tendency toward net immobilization in TD and TD95, mineralization was occurring in all treatments throughout the experiment at varying rates. The growth of the wheat was then dependent on the ability of the plant to outcompete soil microorganisms for the available N. Assuming a constant ability to compete throughout the treatments, this interaction explains the wheat growth in the pots. The pool of available N was lowest in the TD95 pots, so a wheat plant that competed for a proportion of that pool received the least N. As the pool of available N increased, the total N that the plant was able to compete for increased and facilitated greater growth.

Contaminant uptake

While the soil contamination was measured using TPH, wheat grain contamination was measured using 16 PAHs identified by the US EPA (Zelinkova and Wenzl, 2015). These PAHs are commonly used to assess grain safety (Jones et al., 1989; Kobayashi et al., 2008; Ciecierska and Obiedzinski, 2013), as they are a significant threat to human health. Table 7 shows the concentrations of each PAH for the grain samples from N-added pots (NA) and no N-added pots (NN) for each treatment. Notably, the concentration of many compounds was below the detection limit (shown in italics), which fluctuated based

Table 7. Concentration of 16 US EPA priority polycyclic aromatic hydrocarbons (PAHs) in wheat grain grown in soil mixtures from Study 1, divided by those treatments with nitrogen added (NA) and those with no added nitrogen (NN). **BOLD** values indicate **detection** of compound within wheat grain. Italic values indicate the method detection limit for each compound that was not detected. These limits change between due to limits of grain sample size.

PAHs (µg kg^{-1})	TD		TD90		TD70		TD40		TS	
	NA	NN	NA	NN	NA	NN	NA	NN	NA	NN
Acenaphthene	*0.40*	*2.6*	*0.84*	*5.9*	*0.65*	*1.9*	*0.53*	*0.76*	*0.37*	*0.52*
Acenaphthylene	*0.89*	*5.7*	*1.8*	*13.0*	*1.4*	*4.2*	*1.2*	*1.7*	*0.82*	*1.1*
Anthracene	*1.1*	*7.0*	*2.2*	*16.0*	*1.8*	*5.1*	*1.4*	*2.0*	*1.0*	*1.4*
Benzo(a)anthracene	*0.50*	*3.2*	*1.0*	*7.3*	*0.80*	*2.4*	*0.66*	*0.93*	*0.46*	*0.63*
Benzo(a)pyrene	*0.69*	*4.4*	*1.4*	*10.1*	*1.1*	*3.2*	*0.90*	*1.3*	*0.63*	*0.87*
Benzo(b)fluoranthene	**0.44**	*2.7*	*0.88*	*6.2*	*0.69*	*2.0*	**1.0**	**0.91**	*0.39*	*0.54*
Benzo(g,h,i)perylene	*0.81*	**16.7**	*1.7*	*11.9*	*1.3*	**44.4**	*1.1*	*1.5*	*0.74*	*1.0*
Benzo(k)fluoranthene	*0.90*	*5.8*	*1.9*	*13.3*	*1.5*	*4.3*	*1.2*	*1.7*	*0.83*	*1.2*
Chrysene	*0.62*	*4.0*	*1.3*	*9.1*	*1.0*	*2.9*	*0.81*	*1.2*	*0.57*	*0.79*
Dibenz(a,h)anthracene	**2.2**	*4.2*	**2.8**	*9.7*	**1.4**	*3.1*	**6.2**	**3.8**	**1.8**	**5.0**
Fluoranthene	*0.64*	**5.4**	*1.3*	**11.2**	*1.0*	**4.6**	**0.86**	**1.7**	*0.59*	*0.81*
Fluorene	*1.4*	*8.8*	*2.8*	*19.9*	*2.2*	*6.4*	*1.8*	*2.5*	*1.2*	*1.7*
Indeno(1,2,3-cd)pyrene	**37.7**	**14.0**	**51.9**	*15.5*	**26.1**	**28.6**	**78.9**	**47.7**	**26.5**	**59.8**
1-Methylnaphthalene	*1.1*	*7.2*	*2.3*	*16.3*	*1.8*	*5.2*	*1.5*	*2.1*	*1.0*	*1.4*
2-Methylnaphthalene	*1.0*	*6.7*	*2.2*	*15.3*	*1.7*	*4.9*	*1.4*	*2.0*	*0.96*	*1.3*
Naphthalene	*0.56*	*3.6*	*1.2*	*8.2*	*0.90*	*2.6*	**1.0**	*1.0*	*0.51*	*0.71*
Phenanthrene	**0.97**	**16.1**	**2.7**	**33.1**	**1.5**	**14.1**	**1.7**	**1.9**	**0.80**	**1.1**
Pyrene	**0.56**	*2.5*	*0.80*	*5.7*	*0.62*	*1.8*	**0.90**	**1.4**	*0.35*	*0.49*
ΣPAHs (**detected**)	**41.9**	**52.2**	**57.4**	**44.3**	**29**	**91.7**	**90.6**	**57.4**	**29.1**	**65.9**
ΣPAHs (*possible*)	52.5	121	81.0	228	47.2	142	103	76.1	39.5	80.4

on sample size of grain. The possible ΣPAH concentration is then reported as the summation of detections (bold) and the method detection limits. This conservative approach is appropriate when describing food safety, and it avoids dangers involved with omitting non-detects (Helsel, 2006).

The ΣPAH levels in this study were much higher than wheat grain found in the UK (4.3 µg kg^{-1}; Jones et al., 1989), Poland (2.4 µg kg^{-1}; Ciecierska and Obiedzinski, 2013), and California (< 5 µg kg^{-1}; Kobayashi et al., 2008), although they were comparable to wheat grain from agricultural fields in China (80 µg kg^{-1}; Li and Ma, 2016) and Syria (154 µg kg^{-1}; Khalil and Al-Bachir, 2015). Despite these relatively elevated levels, the ΣPAHs may not indicate that this grain is not suitable for human consumption. In fact, no standards for PAHs in foodstuffs exist in the US (ATSDR, 2013). Further, these levels are comparable to those found in other food, such as carrots, which ranged from 48 µg kg^{-1} to 94 µg kg $^{-1}$ (Kipopoulou et al., 1999) and much less than is often found on leafy vegetables, which may reach up to 294 µg kg^{-1} in lettuce (Kipopoulou et al., 1999) or 850 µg kg^{-1} in spinach (Khan and Cao, 2012). Thus, the ΣPAHs are still comparable to food directly consumed by humans on a daily basis (Menzie et al., 1992; Marti-Cid et al., 2008).

Conclusions

The results from these greenhouse studies indicate that TD soils may be able to safely produce grain at similar levels to native TS when supplied with sufficient nutrients and water, although grain protein may be diminished. However, the differences in soil properties, especially biological processes, suggest that soil health in TD soils was not equivalent to TS. These differences may not have been entirely the result of TD treatment, as the TD material was taken from up to 15 m below ground surface and would not be comparable to TS prior to treatment. Nonetheless, until soil health recovers, TD soils may be susceptible to nutrient and water stress that will likely occur under field conditions. Despite substantially less wheat production, mixing the TS with TD soils increased SOC, total N, and, consequently, respiration, which shows that mixing may enhance recovery of soil health. This study identified important trends in wheat growth and soil respiration in controlled conditions, but further research evaluating how TD soils respond to field conditions over successive growing seasons is required to determine how long it takes to return the land to pre-spill levels of crop productivity and soil health.

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CHAPTER 4. A LARGE-SCALE SOIL-MIXING PROCESS FOR RECLAMATION OF HEAVILY DISTURBED SOILS[3]

Abstract

Soil excavation associated with energy production or mineral extraction results in heavily disturbed landscapes that must be reclaimed to avoid long-term economic and environmental losses. A common practice in reclamation of these sites is topsoil replacement across the disturbed area. In some instances, this process requires importing topsoil from another location, known as topsoil transfer, which can be expensive and introduce a new seedbank, insect community, or plant pathogens. This research describes a soil-mixing process for disturbed soils that may be used to reduce costs associated with topsoil transfer and accelerate the recovery of soil function following a large excavation. This process was applied to two disturbed soils: i) crude-oil contaminated subsoil material; and ii) crude-oil contaminated subsoil material that was remediated using ex-situ thermal desorption. These soils were separately mixed with native, non-contaminated agricultural topsoil at 1:1 ratio (by volume). The native, disturbed, and mixed soils were characterized for soil physical, chemical, and biological properties, and statistics indicated that the mixtures were homogenous both spatially and with depth. However, the mixtures were significantly different from both the disturbed materials and native topsoil, primarily driven by changes in soil organic carbon, plant available nutrients, and biological activity. These results suggest that this mixing process can be used for soil reclamation at large-scale excavation sites to both reduce project costs and enhance recovery of soil parameters.

Introduction

Extraction of natural resources, including fossil fuels and other minerals, provides energy resources and raw materials crucial to modern society, as well as providing economic benefits. However, the processes of attaining these fuels can lead to heavily disturbed landscapes. Coal mining and

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quarrying, for example, often entail excavation of massive pits and stockpiling of soils for many years. This excavation destroys existing soil structure (Indorante et al., 1981), interrupts pore networks (Guebert and Gardner, 2001), decreases soil organic matter (SOM; Wick et al., 2009), and inhibits microorganisms (Miller et al., 1985). Stockpiling soil can also reduce SOM (Wick et al., 2009), alter nutrient cycling (Williamson and Johnson, 1990), and hinder vegetation reestablishment (Stahl et al., 2002), although many techniques have been developed to reduce the severity of those effects. Similarly, oil extraction requires reclamation of well pads, roads, and pipelines; further, accidental releases of crude oil can require remediation projects that may also disrupt soil function (O'Brien et al., 2017a). These remediation techniques, such as chemical oxidation, landfarming, or thermal desorption, also alter soil properties (Besalatpour et al., 2011; Villa et al., 2008), including pH, SOM, and microbial community dynamics. Accordingly, these projects can reduce topsoil production potentials (Boyer et al., 2011; Shrestha and Lal, 2011; Wick et al., 2009) by introducing subsurface material (e.g., mine tailings, remediated material) to the soil surface (Soon et al., 2000), which negatively affect soil function and require further management to reclaim or restore the land.

Several strategies are available to manage these disturbed sites. First, managers may choose not to take any restorative action and leave the mine spoils, deteriorated topsoil, or subsoil in place (Sena et al., 2014). This approach, natural attenuation, is the least costly, although it may not comply with regulations, and it may not be accepted by public opinion. This approach also takes a very long time compared to other approaches, but it can eventually restore soil function. Similarly, soils can be remediated using a variety of techniques (O'Brien et al., 2017a) and then replaced. More commonly, topsoil is replaced across the disturbed area. Applying topsoil immediately improves soil function (Larney et al., 2012), although not always to pre-disturbance levels (Mummey et al., 2002). This topsoil may be stripped from the original site and stockpiled until reclamation, or it may be purchased and transferred from another location. Purchasing topsoil may be too expensive or unavailable in some instances, and it is accompanied by a risk of introducing a weed seedbank, an undesirable insect community, or plant pathogens. Further, caution must be used in selecting imported topsoil to avoid exposing the soil to trace elements or heavy metal loading. Additionally, transferring topsoil from another location simply creates a topsoil deficit elsewhere, effectively relocating the issue but not solving it. Finally, organic amendments, wastes, or composts may be incorporated into the disturbed material to increase SOM and improve biological communities (Stolt et al., 2005).

This research describes an approach that integrates these ideas, in which native topsoil is mixed into both contaminated and remediated disturbed soil materials. The disturbed material in this research was taken from a remediation site of a crude-oil pipeline leak that contaminated subsurface material down to 15 m below the surface. This study incorporates both the crude-oil contaminated material, as well as contaminated material that has been remediated using ex-situ thermal desorption. These two disturbed materials were separately mixed with local, non-contaminated agricultural topsoil. Given that the topsoil was locally available from the remediation project, the cost of purchasing and transporting the material was avoided, and the risk of introducing a seedbank of weeds or plant pathogens via local topsoil is low.

Several researchers have identified some benefits of mixing topsoil with disturbed material. By adding SOM-rich material, SOM of the overall mixture is increased, which is associated with improved biomass production and hydrologic function (Merino-Martin et al., 2017; Larney and Angers, 2011), as well as microorganism dehydrogenase activity (Smart et al., 2016). Topsoil mixing into the disturbed material also allows these benefits to extend deeper in the profile, which is vital for successful reclamation (Chenot et al., 2017; Larney et al., 2012). Thus, using topsoil as a mixing agent both aids in recovery of soil function (O’Brien et al., 2017b; Callaham et al., 2002; Roh et al., 2000) and also reduces the amount of topsoil needed for replacement, which may be vital in projects with topsoil deficits (Merino-Martin et al., 2017; Carson et al., 2014). To date, these benefits of topsoil mixing have been primarily identified at the laboratory and greenhouse level. Thus, this research is valuable in helping to identify a process by which these benefits can be attained that is i) applicable at a large scale and ii) results in uniform soil mixing.

The aim of this research was to assess the homogeneity of research plots constructed using a large-scale mixing technique applied near an active soil remediation project. This determination was made by analyzing soil characteristics of the soil mixtures and comparing them to unmixed samples at four different depths. Multivariate analyses were employed to compare both homogeneity within each treatment and differences between the treatments. Identifying homogeneity within the plots indicates that the added topsoil was spread evenly throughout, which maximizes the benefits of mixing. Additionally, this work provides a framework for separating treatment effects of soil mixing from the natural variability of soil properties. This study provides vital information on understanding the effects of excavation and reclamation on soil parameters, as well as identifies soil-mixing as a viable alternative to current practices.

Materials and Methods

Study area and soil materials

This research took place adjacent to an active remediation site in Mountrail County, ND, USA (48°31'35.4"N, 102°51'25.72"W). The site is currently using thermal desorption to treat a pipeline spill that released Bakken crude oil into an agricultural field and underlying subsoil. Research plots were constructed near the site using three different soils to create five treatments. Non-contaminated, native topsoil acted as a control (A; Treatment 1). The A is mapped as Williams-Zahl loams (Williams: fine-loamy, mixed, superactive, frigid Typic Argiustolls; Zahl: fine-loamy, mixed, superactive, frigid Typic Calciustolls) (NRCS, 2015). It was excavated and stockpiled for several months prior to plot construction during the course of the remediation project. Topsoil stockpiles were each approximately 9 m tall, (90 m long by 30 m wide at the highest point), with 2H:1V slopes, and they were not seeded. Thus, the A used in the plots was the original soil, and it received no additional treatment other than the excavation and replacement. Crude oil-contaminated subsurface soil material was taken from the stockpile of untreated material in the remediation project (SP; Treatment 2). The SP is a mixture of soils taken across the entire width and depth of the site, and was initially passed through a 10 cm screener (R155 Screener, McCloskey International, Keene, Ontario) to ensure a uniform material. The SP was treated by an RS 40 Thermal Desorption/Oxidation unit at 350 °C for 10 min to create thermal desorption-treated subsurface material (TD; Treatment 3). Both SP and TD materials were originally excavated on-site, but they were a mixture of contaminated material from down to 15 m below ground surface; thus, the original depth of these materials is not identified. Although neither SP nor TD material originated from the zone of soil genesis, for ease of reference, these materials will be referred to hereafter as "SP soil" and "TD soil". The final two treatments were mixtures created using the A, TD, and SP soils: 1:1 mixture (by volume) of A and SP (SPA; Treatment 4) and 1:1 mixture (by volume) of A and TD (TDA; Treatment 5).

Mixing process and plot construction

The soil mixtures, SPA and TDA, were created by the following process. Piles of each soil type (A, SP, and TD) were staged adjacent to the plot area for construction. Two material types were added into a screener in alternating 0.6 m^3 excavator bucket-loads (336E Hydraulic excavator, Caterpillar Inc., Peoria, Illinois). For example, one bucket of A was placed into the hopper for the screener, followed by one bucket of TD (or SP), followed by one bucket of A, and so forth (Figure 12, a). After passing through the initial screener, the mixed soil passed through a second screener and moved via material stacker (ST80 Wheeled stacker, McCloskey International) approximately 4.5 m into the air before being deposited into a staging pile of mixed soil (Figure 12, b).

Thirty plots were constructed, with each treatment repeated twice in each of three replications. Each plot holds approximately 230 m^3 of soil (17 m x 15 m x 0.9 m). The soil was loaded from the staging piles into dump trucks (730 Ejector articulated dump truck, Caterpillar Inc.) that hauled the soil into each plot and dumped the material freely onto the prepared area (Figure 12, b and c). Each plot required 25 truckloads of soil, and they were constructed in sequence such that the dump trucks did not drive over any completed plots. Once the material was deposited in each plot, it was spread using a tracked vehicle with an excavator bucket (336E Hydraulic excavator, Caterpillar, Inc.) to make the plots as even as possible (Figure 12, d).

Sampling procedure and analyses

Plot construction was completed in November 2015 (Figure 13), and core sampling occurred in early December 2015. The plots were sampled as soon as possible after construction to ensure that measurements reflected the conditions of each plot due to mixing and did not include any natural recovery of soil characteristics. All soil sampling was done in a nested 12 m x 12 m square to avoid border areas that may be subject to mixing between treatments. A Giddings soil probe (Giddings Machine Company, Inc., Windsor, Colorado) was used to take four cores to 0.9 m depth from each plot. The cores were taken at three points systematically in diagonal paths across each plot, wherein each plot was divided into thirds. Then, one core was taken from the northern third, two from the middle third, and one from the southern third. One core taken from the middle third was divided into four depths (0-15 cm, 15-30 cm, 30-60 cm, 60-90 cm) and sent to a private laboratory (Pace Analytical Services, Inc., St. Paul,

Figure 12. Photographs showing the soil mixing process. Pane a) shows two different soil materials, A and TD, prepared to be placed in alternating bucketloads to the screeners. Soils were taken from the staging pile (b) via trucks to be dumped into plots (c). Plots were smoothed with an excavator bucket (d). The stark color differences of three plots with different materials (A: native, non-contaminated topsoil; TD: crude oil contaminated subsoil material treated by thermal desorption; SP: crude oil contaminated subsoil material) are shown in pane e). The finalized plots were completely filled and leveled to match topography of the surrounding area.

Minnesota) and analyzed for total petroleum hydrocarbons (TPH; Table 8). Sampling materials were wiped clean with towels and decontaminated using methanol after each sample. The remaining three cores were divided at the same depths, air-dried at 25 °C, and ground to pass through a 2 mm sieve. Samples from these three cores were analyzed by methods shown in Table 8.

Additionally, separate soil samples were taken for analysis of soil biological parameters. These samples were taken with a hand probe (4 cm in diameter) from six randomly placed locations within each plot. These samples were separated into two depths, 0-15 cm and 15-30 cm, and the six samples from each plot were combined into one bag for each depth per plot. The biological parameters measured are also shown in Table 8.

Figure 13. Aerial photograph of completed soil plots. Each plot (17 m x 15 m x 0.9 m) holds one of the five treatments: A) native, non-contaminated topsoil; TD) crude oil contaminated subsoil material treated by thermal desorption; SP) crude oil contaminated subsoil material; TDA) 1:1 mixture, by volume, of A and TD; and SPA) 1:1 mixture, by volume, of A and SP. Five labelled plots show that they are readily distinguished from one another by color differences.

Statistical analyses

Multivariate analyses were employed to evaluate the effectiveness of soil mixing; thus, no statistical analyses were performed on any variable individually. A multivariate analysis of variance (MANOVA) of the physical and chemical parameters observed in the soil or mixture samples was conducted to identify if core, depth, or treatment interactions existed. Upon finding no significant difference between core for soil characteristics listed in Table 9, the data were pooled by treatment and depth for combined analysis with soil biological parameters. A two-way MANOVA was performed on this combined data using treatment and depth as factors. Pillai's trace test statistic was used on all MANOVA

Table 8. List of variables quantified in the research plots, given with the abbreviations shown in the principal components analyses. The method for quantifying each variable is also given. Only the variables shown above the bold line were used in the first PCA, while all variables were included in the second.

Variable	Abbrev.	Units	Method	Reference
Plant available water	PAW	$cm^3\ cm^{-3}$	Pressure plate extractor	Dane and Hopmans, 2002
Specific surface area	SSA	$m^2\ g^{-1}$	EGME[a] retention	Pennell, 2002
% Sand	s	$g\ kg^{-1}$	Hydrometer	Gee and Or, 2002
% Silt	si	$g\ kg^{-1}$		
% Clay	c	$g\ kg^{-1}$		
Inorganic carbon	IC	$g\ kg^{-1}$	Primacs TOC Analyzer	Skalar Analytical, B.V.
Organic carbon	SOC	$g\ kg^{-1}$		
‡ pH	pH		1:1 extract	Watson and Brown, 1998
‡ Electrical conductivity	EC	$dS\ m^{-1}$	1:1 extract	Whitney, 1998a
Inorganic nitrogen	N	$mg\ kg^{-1}$	Summation of NO_3^- and NH_4^+	Mulvaney, 1996
‡ Nitrate	NO_3^-	$mg\ kg^{-1}$	0.2 M KCl extraction with Cd reduction	
‡ Ammonium	NH_4^+	$mg\ kg^{-1}$	2N KCl extraction with Timberline NH_4 analyzer	
‡ Phosphorus	P	$mg\ kg^{-1}$	Olsen method	Frank et al., 1998
‡ Potassium	K	$mg\ kg^{-1}$	Ammonium acetate extract determined with optical emission ICP	Warncke and Brown, 1998
‡ Calcium	Ca	$mg\ kg^{-1}$		
‡ Magnesium	Mg	$mg\ kg^{-1}$		
‡ Sodium	Na	$mg\ kg^{-1}$		
‡ Zinc	Zn	$mg\ kg^{-1}$	DTPA sorbital method with optical emission ICP	Whitney, 1998b
‡ Iron	Fe	$mg\ kg^{-1}$		
‡ Manganese	Mn	$mg\ kg^{-1}$		
‡ Copper	Cu	$mg\ kg^{-1}$		
‡ Chlorine	Cl	$mg\ kg^{-1}$	Hg (II) thiocyanate method	Gelderman et al., 1996
*Total petroleum hydrocarbons	TPH	$mg\ kg^{-1}$	EPA 8015 modified with silica gel	adapted from USEPA, 1996
Nitrate reductase	NO_3.red	$\mu g\ NO_2\text{-}N\ g^{-1}$ soil 24 h^{-1}	Determine on colorimetric basis using Spectrophotometer[b]	Abdelmagid and Tabatabai, 1987
Urease	Urease	$\mu g\ NH_4\text{-}N\ g^{-1}$ soil 2 h^{-1}		Kandeler and Gerber, 1988
Ammonium oxidation	NH_4.ox	$\mu g\ NO_2\text{-}N\ g^{-1}$ soil 5 h^{-1}		Berg and Rosswall, 1985
Potentially mineralizable nitrogen	PMN	$mg\ NH_4^+\text{-}N\ g^{-1}$ soil 7 d^{-1}	7 d anaerobic incubation	Moebius-Clune et al., 2016
Active carbon	AC	$mg\ C\ kg^{-1}$ soil	$KMnO_4$ oxidation	Moebius-Clune et al., 2016

‡ Analyses conducted at Agvise Laboratories, Northwood, North Dakota.

* Analyses conducted at Pace Analytical Services Inc., St. Paul, Minnesota

[a] EGME: ethylene glycol monoethyl ether

[b] Spectrophotometer (Thermo Spectonic 20D+, Thermo Fisher Scientific, Madison, WI, USA)

because the data displayed some collinearity (Rencher and Christensen, 2012). MANOVAs were conducted with R software using the *stats* package (R Core Team, 2016).

Principal components analysis (PCA) was performed on the correlation matrix of the complete dataset of 360 observations using 20 physical and chemical variables. A second PCA was performed on the correlation matrix following the addition of 6 biological parameters. Both PCAs were performed on the correlation matrices, which are scale invariant, due to the variety of scales, variances, and units among the measured parameters (Rencher and Christensen, 2012). PCA biplots were constructed showing each data point identified by treatment, and abbreviations of variable names were plotted based on PCA loadings scores. PCA was performed with R software using an unconstrained redundancy analysis in the *vegan* package (Oksanen et al., 2016).

For this analysis, no variables were excluded because of high correlations. Since PCA identifies latent structures in the data to describe variability, highly correlated variables are often excluded to avoid weighting the analysis with several variables describing the same latent structure. However, the correlations in this data do not describe the same underlying processes for each PC. For example, although plant available NO_3-N, NH_4-N, and P may all be correlated with SOM, the biochemical processes that govern the cycling of these nutrients are not the same (Mengel and Kirkby, 2001). Furthermore, including all variables, even highly correlated ones, is especially valuable when describing disturbed soil material, since the disturbance may not affect all parameters or processes in the same way.

Results

Physical and chemical variables

Mean values and ranges for all of the measured soil parameters used in the first PCA are shown in Table 9. As expected, soil mixing tended to result in intermediate values of the two starting materials for most parameters. For example, the mean SOC of A was 21 g kg^{-1}, while TD was 3 g kg^{-1}; the mixture (TDA) had an SOC of 11 g kg^{-1}. The MANOVA determined that these variables did not significantly differ among cores ($p = 0.39$), depth ($p = 0.10$), or any (either two-way or three-way) interaction term ($p = 0.64$ and higher), but the treatment factor was significant ($p < 0.001$).

Figure 14 shows the biplot created from the PCA conducted on the 20 physical/chemical variables across the three cores and four depths. Because the MANOVAs identified treatment as the only significant factor, samples on the PCA biplot are displayed by treatment. The PCA consolidated as much variability as possible into two Principal Components (PC1 and PC2) for each PCA. In the first PCA, two axes explained 68% (PC1: 55%; PC2: 13%) of the variability among the 20 variables included (Figure 14). Each soil sample is plotted in relation to those components; thus, proximity implies similarity between samples, and greater distance implies dissimilarity. Additionally, the text annotations of soil variables indicate the loadings from PC1 and PC2, so they are meaningful in interpreting spatial orientation.

Inclusion of biological parameters and contaminant concentration

Mean values and ranges for all of the additional soil parameters used in the second PCA are shown in Table 10. Similar to the physical and chemical parameters shown in Table 9, the values in the mixtures are typically intermediate values compared to the two starting materials. Notably, the biological parameters provided the starkest contrast between the A and either the SP or TD, as nitrate reductase, urease, and ammonium oxidation activities were almost non-existent in the disturbed materials. The MANOVA with the additional parameters for only the upper two depths also indicated a treatment difference ($p < 0.001$) but that no significant differences occurred with depth ($p = 0.13$) or treatment*depth ($p = 0.53$) interaction, which further indicates homogenous mixing.

Figure 15 shows the PCA from all 26 physical, chemical, and biological variables across two depths. In this PCA, two axes explained 76% (PC1: 62%; PC2: 14%) of the variability among the variables included (Figure 15). Compared to the first PCA (68%), the second PCA (76%) identified greater group separation and described more variation, while the trends of within- and between-treatment variation were the same. The A samples were the most spread out, while the TD had the least within-treatment variability. SP samples showed a greater spread along PC2, likely due to the wide variability in the TPH values (Table 10). Notably, both mixtures again showed intermediate within-treatment variability, and they were both spatially oriented in the midpoints between A and TD or SP, respectively.

Table 9. Selected summary statistics for the 20 physical/chemical variables included in the first Principal Components Analysis. Mean value (with standard deviation) and range of each variable are shown, separated by treatments. Treatments are: A) native, non-contaminated topsoil; TD) contaminated subsoil material treated by thermal desorption; SP) crude oil contaminated subsoil material; TDA) 1:1 mixture, by volume, of A and TD; and SPA) 1:1 mixture, by volume, of A and SP. Data are pooled by core and depth.

Treatment	**A**		**TDA**		**TD**		**SPA**		**SP**	
Variable *(unit)*	Mean (sd)	Min - Max	Mean (sd)	Min - Max	Mean (sd)	Range	Mean (sd)	Min - Max	Mean (sd)	Min - Max
PAW *(cm^{3} cm^{-3})*	11 (1.2)	8.6 - 14	11 (1.1)	8.8 – 14.0	10 (1.0)	7.6 – 13	11 (1.2)	7.9 – 13	11 (1.2)	5.3 – 13
SSA *(m^{2} g^{-1})*	84 (8.1)	66 - 106	86 (6.7)	56 – 100	92 (9.4)	70 - 107	98 (8.4)	78.0 – 114	104 (8.7)	72 – 124
Sand *(g kg^{-1})*	455 (29)	327 – 517	451 (15)	398 – 488	434 (19)	398 – 476	423 (19)	321 – 453	389 (12)	340 – 418
Silt *(g kg^{-1})*	327 (21)	266 – 407	321 (18)	272 – 362	326 (25)	193 – 383	325 (19)	285 – 413	345 (19)	295 – 389
Clay *(g kg^{-1})*	219 (27)	168 – 279	228 (17)	181 – 254	239 (22)	198 – 356	252 (16)	219 – 297	266 (15)	232 – 301
IC *(g kg^{-1})*	3 (2)	0 - 7	11 (3)	4 – 20	16 (1)	14 - 19	11 (3)	6 - 25	16 (1)	13 - 18
SOC *(g kg^{-1})*	21 (4)	13 - 29	11 (2)	4 - 17	3 (1)	1 - 6	11 (3)	2 - 18	5 (1)	2 - 8
pH	7.4 (0.2)	6.9 - 7.8	7.8 (0.1)	7.6 - 8.3	8.1 (0.1)	8 - 8.3	7.8 (0.2)	7.4 - 8.8	8.1 (0.1)	7.9 - 8.3
EC *(dS m^{-1})*	0.3 (0.1)	0.2 - 0.4	0.6 (0.1)	0.4 - 0.8	0.8 (0.2)	0.6 - 1.3	0.7 (0.1)	0.4 - 1.1	1.0 (0.2)	0.5 - 1.5
N *(mg kg^{-1})*	28 (5.7)	14 – 43	19 (2.3)	13 – 24	8.5 (1.3)	5.3 – 12	11 (3.9)	3.8 – 20	5.2 (1.8)	2.1 – 13
P^{a} *(mg kg^{-1})*	9 (1.9)	4.0 – 13	7.0 (1.3)	2 – 13	3.3 (1.5)	2.0 - 14	4.9 (1.6)	2.0 – 9.0	2.1 (0.7)	2.0 – 7.0
K *(mg kg^{-1})*	248 (20)	204 – 315	227 (16)	167 - 269	193 (9)	172 - 215	192 (24)	133 - 246	148 (12)	108 - 171
Ca *(mg kg^{-1})*	3220 (505)	2340 - 4840	4360 (201)	3660 - 4810	4710 (14)	4400 - 5090	4300 (283)	3500 - 4850	4550 (146)	3920 - 4880
Mg *(mg kg^{-1})*	636 (69)	490 – 814	670 (106)	556 - 1347	691 (40)	614 - 774	861 (182)	722 - 1863	998 (80)	776 - 1165
Na *(mg kg^{-1})*	17 (1.9)	13 – 23	56 (9.4)	30 – 102	114 (17)	74 - 145	55 (13)	35 - 107	95 (18)	40 – 125
Zn *(mg kg^{-1})*	0.8 (0.2)	0.4 - 1.5	0.8 (0.1)	0.4 - 1.1	0.8 (0.1)	0.6 - 1.1	0.5 (0.1)	0.2 - 0.8	0.4 (0.2)	0.2 - 1.9
Fe *(mg kg^{-1})*	49 (15)	26 – 90	25 (3.8)	15 – 42	10 (1.1)	7.5 – 13	24 (7.0)	7.8 – 41	11 (2.1)	5.8 – 20
Mn *(mg kg^{-1})*	51 (44)	7.0 – 202	29 (12.7)	5.0 - 99	25 (4.9)	11 - 37	17 (6.5)	1.0 – 36	12 (4.8)	8.0 – 31
Cu *(mg kg^{-1})*	1.2 (0.2)	0.9 - 1.8	1.2 (0.1)	1.1 – 1.6	1.3 (0.1)	1 - 1.5	1.2 (0.1)	1.0 - 1.6	1.3 (0.3)	1.0 - 2.3
Cl *(mg kg^{-1})*	1.9 (0.6)	1 - 4.5	10 (2)	3.5 – 16	20 (2.5)	11 - 26	5.2 (1.3)	2 - 9	8.9 (1.7)	5 - 12

[a] Olsen P

Table 10. Selected summary statistics for the 6 additional chemical/biological variables included in the second Principal Components Analysis. Mean value (with standard deviation) and range of each variable are shown, separated by treatments. Treatments are: A) native, non-contaminated topsoil; TD) contaminated subsoil material treated by thermal desorption; SP) crude oil contaminated subsoil material; TDA) 1:1 mixture, by volume, of A and TD; and SPA) 1:1 mixture, by volume, of A and SP. Data are pooled by depth.

Treatment	**A**		**TDA**		**TD**		**SPA**		**SP**	
Variable *(unit)*	Mean (sd)	Min - Max	Mean (sd)	Min - Max	Mean (sd)	Range	Mean (sd)	Min - Max	Mean (sd)	Min - Max
TPH *(mg kg^{-1})*	22 (8.9)	0 - 32	100 (33)	44 - 166	221 (49)	142 – 308	705 (324)	144 - 1344	1470 (546)	554 - 2354
NO_3.red[a]	3.5 (0.9)	2.3 – 5.2	1.9 (0.5)	1.1 - 2.8	0.1 (0.1)	0 - 0.4	4.6 (1.6)	2.2 - 7.4	0.4 (0.2)	0.1 - 0.9
Urease[b]	56 (16)	28 – 85	18 (4.5)	10 - 25	1.5 (1.8)	0 - 4.8	27 (9.4)	17 - 46	4 (2.3)	0 - 7.2
NH_4.ox[c]	1.9 (0.3)	1.5 – 2.3	0.8 (0.2)	0.5 - 1	0 (0.1)	0 - 0.2	0.5 (0.1)	0.3 - 0.7	0 (0)	0 - 0.1
PMN[d]	15 (3.3)	10 - 23	6.5 (2.2)	4.2 - 9.9	0.1 (0.2)	0 - 0.6	13 (3.9)	6.6 - 20	0 (0)	0 – 0
AC *(mg kg^{-1})*	396 (39)	321 – 442	274 (44)	196 - 380	208 (32)	143 - 244	284 (54)	228 - 410	135 (27)	80 – 174

[a] Nitrate reductase *(μg NO_2-N g^{-1} soil 24 h^{-1})*

[b] *(μg NH_4-N g^{-1} soil 2 h^{-1})*

[c] Ammonium oxidation *(μg NO_2-N g^{-1} soil 5 h^{-1})*

[d] Potentially mineralizable nitrogen *(mg NH_4^+-N g^{-1} soil 7 d^{-1})*

Discussion

This research was conducted to determine the homogeneity of research plots constructed using a large-scale mixing technique with native topsoil, remediated soil, and crude oil-contaminated soil. Spatial homogeneity was determined because no differences in soil characteristics were identified based on spatial position within each plots (i.e., core factor in the MANOVA). Similarly, homogeneity by depth was determined since no differences in soil characteristics were identified based on depth of measurement within the samples (i.e., depth factor in the MANOVA). This homogeneity across space and with depth is reinforced by the fact that no interactions (either two-way or three-way) were significant among the samples. Thus, the only statistically significant measure of group separation identified in these samples was by treatment. While the MANOVA identified homogeneity in these research plots, the PCA biplots allow for further description of variability in soil characteristics of soil samples, both within-treatment and between-treatments.

Within-treatment variability

Within-treatment variability is a valuable assessment for the soil mixing process because it evaluates homogeneity for a given soil treatment, and it can be described by considering the spatial relationships of samples of the same treatment on the biplots. Despite originating from a wide range of depths, both TD and SP are very tightly grouped (Figure 14), indicating they are the most homogenous treatments. This finding is likely due to the extensive material handling of these two groups, as well as their similar origins. Soils of both groups were excavated, hauled to a stockpile, tilled regularly, and screened two (SP) or three (TD) times prior to plot construction. Conversely, the A samples display the most within-treatment variability. The A samples were simply excavated, stockpiled, and replaced, so their properties most closely resemble those of natural soil formation. Natural soil formation is typified by spatial variability due to micro-scale topography, hydrology, and biological interactions (Burke et al., 1999), so they may be expected to be more variable than the screen materials. Notably, the samples from both soil mixtures are grouped with intermediate distances within each treatment compared to the A and TD or A and SP. This intermediate orientation suggests that A has been homogenously mixed with the SP and TD, respectively, which is vital to ensure that the benefits of soil mixing are evenly distributed throughout each plot (O'Brien et al., 2017b; Smart et al., 2016; Callaham, Jr., et al., 2002).

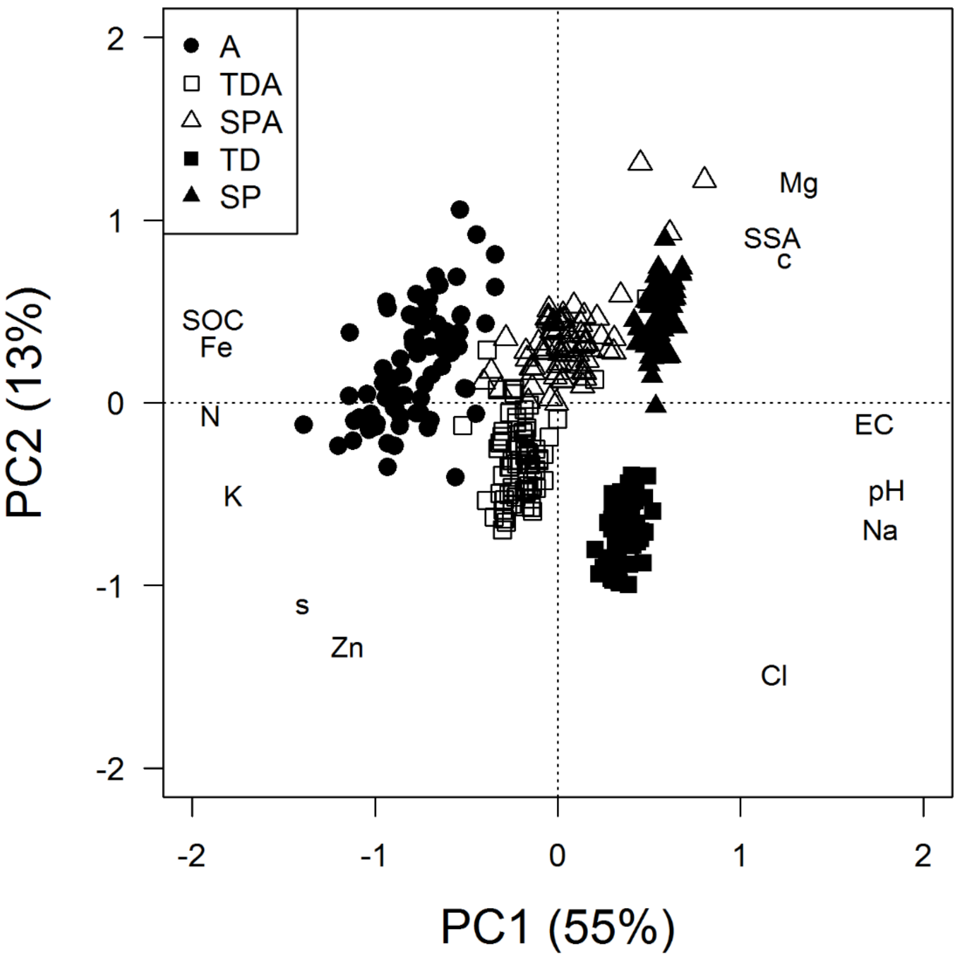

Figure 14. Principal components analysis of 20 physical and chemical soil properties with loadings identified by text annotations of each properties abbreviation. Samples are identified by treatment, which are A) native, non-contaminated topsoil; TD) crude oil contaminated subsoil material treated by thermal desorption; SP) crude oil contaminated subsoil material; TDA) 1:1 mixture, by volume, of A and TD; and SPA) 1:1 mixture, by volume, of A and SP.

Between-treatment variability

The between-treatment variability is also evident in both Figure 14 and Figure 15, and it can be described by the spatial relationship of samples from different treatments on the biplots. Notably, since the x-axis describes the most variability (55%), spatial orientation on that axis is more descriptive of dissimilarity than on the y-axis. Thus, the A samples differ more from the TD and SP samples than those two differ from one another. The loadings indicate that A samples are associated with SOC, N, P, and K, which are all generally correlated with SOM and representative of typical topsoil function of biomass production, nutrient cycling, and other biological activity (Paul, 2016; Larney and Angers, 2011; Lal, 2006). The wide separation on the x-axis is due to very low values of SOC in the both the TD and SP. Very little SOC is expected at the depths from which SP samples originated, and thermal desorption-treatment reduces it even further (O'Brien et al., 2016; Sierra et al., 2016). Conversely, the TD and SP have higher pH and EC values. Soil pH can increase following thermal desorption-treatment since the decrease in SOM results in a loss of organic acids (Sierra et al., 2016; Terefe et al., 2008). Further, the combustion of SOM releases basic cations that can increase EC. High pH and EC are also found in the SP soils, although the cause of these higher values is likely more dependent on parent material than any soil handling or management. Although the y-axis explains less variability (13%), it does serve to separate the SP from the TD. The SP was characterized by higher clay content, SSA, and Mg, while TD showed higher Na and Cl contents. With only a few outliers, most of the soil mixture samples fall directly between the A and TD or A and SP, respectively, on both axes. This orientation of these samples indicates a consistent, uniform mixing process that is representative of the 1:1 mixture relationship.

Inclusion of biological parameters and contaminant concentration

The first PCA offers a framework with which to evaluate the effectiveness of the mixing process, but it did not include any biological parameters or contaminant concentration that can be vital indicators of reclamation success. Due to the cost and time investment associated with the analyses, biological parameters, as well as TPH, were only analyzed for two depths (0-15 cm, 15-30 cm). These depths were chosen because most microbial activity occurs closer to the soil surface (Gelsomino and Azzellino, 2011; Blume et al., 2002). By assessing biological activity and contaminant concentration, the second PCA (Figure 15) is more reflective of how overall soil function may be improved by the soil mixing process (Ferris and Tuomisto, 2015). The mixing process produced plots that were much more similar in physical and chemical characteristics than they were from a biological perspective, as evidenced by greater distances between treatments in Figure 15 than in Figure 14. The cluster of biological parameter loadings close to the A samples highlights the necessity of recovering biological activity following TD treatment, and the ability of soil mixing to begin that recovery. This finding also reinforces the need to understand how soil physical, chemical, and biological factors can dictate soil function and, ultimately, determine reclamation success (O'Brien et al., 2017a).

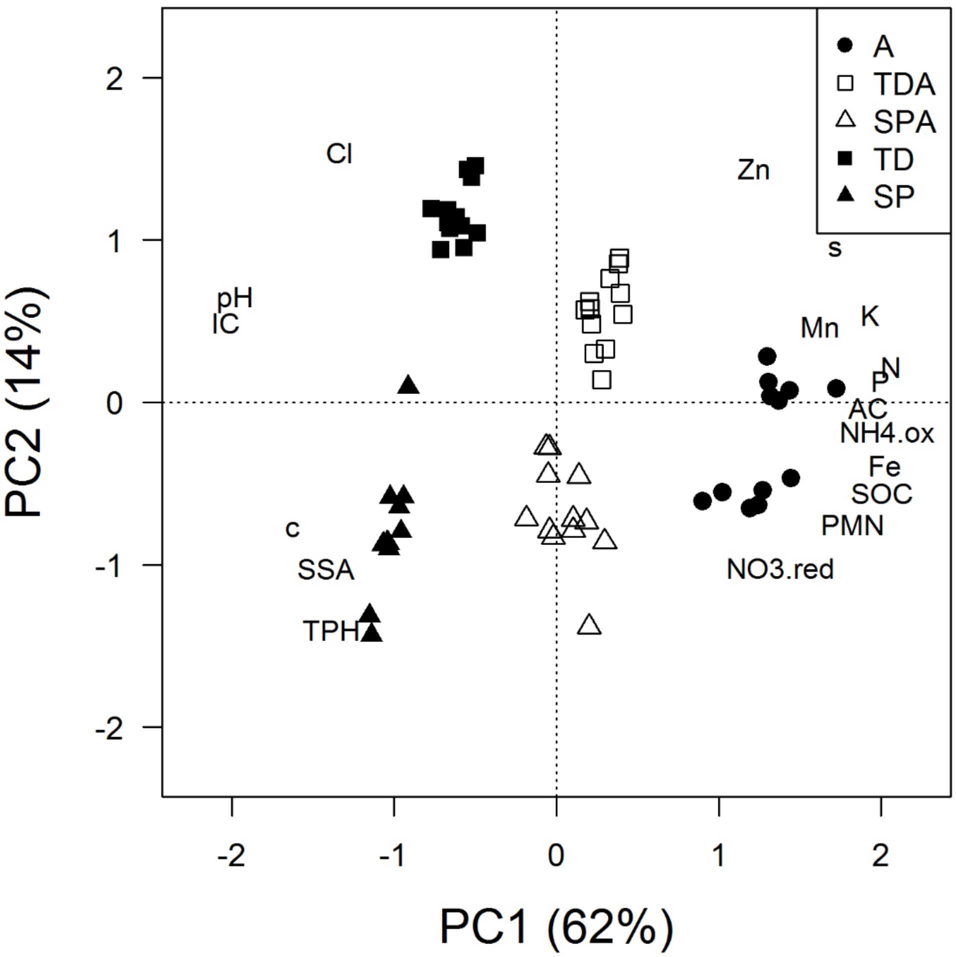

Figure 15. Principal components analysis of 26 physical, chemical, and biological soil properties with loadings identified by text annotations of each property's abbreviation. Samples are identified by treatment, which are A) native, non-contaminated topsoil; TD) crude oil contaminated subsoil material treated by thermal desorption; SP) crude oil contaminated subsoil material; TDA) 1:1 mixture, by volume, of A and TD; and SPA) 1:1 mixture, by volume, of A and SP.

This study included soil mixing using contaminated material for two reasons. First, the contaminated material offered another example of how the soil-mixing process may uniformly distribute the A and SP in a research plot, in addition to the thermal desorption-treated material. Second, the research plots will be used in future research to determine if mixing topsoil together with contaminated material increases the rate of degradation of TPHs. Notably, while some specific petroleum hydrocarbons are regulated individually, neither the USEPA nor the state of North Dakota have existing guidelines for acceptable levels of TPHs in soils (ATSDR, 1999), so contaminated sites are dealt with on a case-by-case basis. Nonetheless, in many cases, mixing contaminated material with uncontaminated material may not be an appropriate course of action. Under Resource Conservation and Recovery Act regulations, diluting (i.e., mixing) soils contaminated with hazardous materials is not an acceptable treatment option (RCRA, 1976).

Implications for soil mixing in reclamation

These biplots can also be useful as a tool for visualizing reclamation success over time, with the assumption that success is creating a soil system most similar to the native, non-contaminated topsoil. In theory, the samples from the different treatments will grow closer together as time progresses, indicating that different soil treatments are becoming more similar. In this case, the mixtures are already moving towards the A samples, suggesting that soil mixing may accelerate recovery of the parameters included in this study. However, even with comprehensive management, reaching a reference state can take decades (Chenot et al., 2017). As shown by the loadings, the mixtures are typified by characteristics that may be more representative of a reclaimed, functioning soil system than the TD or SP soils. Further, soil mixing encouraged biological activity, which can be expected to enhance the rate of recovery, as well.

For appropriate management decisions, both the within- and between-treatment variability must be considered on the full range of soil samples. The within-treatment variability of the A is so large that some of the samples are more similar to the soil mixtures than to other A samples. This finding could lead to the false conclusion that reclamation was successful (i.e., TDA and SPA matched A after only one season) when the whole data set clearly shows between-treatment separation of these groups. Thus, this example typifies the need for comprehensive soil sampling and holistic analysis of data to assess the effectiveness of reclamation practices.

The findings of this research suggest that this mixing process may be applicable across a range of situations, especially in those situations in which the disturbed material is lacking in SOM or biological activity. The homogeneity of the mixtures in this project are likely due to the general similarities in the original materials used. Notably, the greatest difference between A and the TD/SP was SOC, with only minor differences in pH, EC, and available heavy metals. However, the incorporation of topsoil into disturbed or subsurface soil material with drastically different characteristics, especially texture or pH, may produce different results. Nonetheless, mixing with topsoil can jumpstart the soil reclamation process by both moving the starting point much closer to the final goal and increasing the rate at which the goal may be achieved.

Conclusions

This study examined the ability of a large-scale soil mixing process to produce homogeneous research plots by analyzing spatial and depth-dependent variation of 26 soil characteristics. The MANOVAs and PCAs showed that treatments were homogenous both spatially and with depth, although the treatments differed from one another. Notably, the properties of the soil mixtures, TDA and SPA, were proportional to the A and TD/SP at the 1:1 ratio in most soil properties, and their spatial orientations were intermediate in the PCA. Inclusion of biological parameters reinforced these trends. Analyzing physical, chemical, and biological parameters is a useful way to gain understanding of how the process can be beneficial in soil reclamation. Using these soil parameters as a proxy for restoring soil function, this research indicates that soil mixing may be a promising approach to improving TD-treated or lightly contaminated material, as well as excavated subsoil material. These findings show that function likely would not be initially restored to the level of A, but the mixing process can improve disturbed/subsurface soil material enough to return to a variety of land uses. Mixing at a 1:1 ratio can double the quantity of suitable material available for reclamation, although the quality of the mixed material may not be as high as native topsoil. Thus, the application of this practice should be determined on a case-by-case basis, as the goals of the project must be considered. Nonetheless, the process may provide a less costly way to reclaim disturbed areas and promote the recovery of soil function.

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CHAPTER 5. DAYTIME SURFACE ENERGY FLUXES OVER SOIL MATERIAL REMEDIATED USING THERMAL DESORPTION

Abstract

Remediation efforts to reduce contaminant concentration in soils often also alter soil properties. Since these alterations can affect the capacity of soil to function, their extent and magnitude may dictate future land use. This study addresses the suitability of soils for agricultural production after being remediated using ex situ thermal desorption by quantifying the daytime (7:00 – 20:00) surface energy balance prior to the growing season. The energy balance was quantified using micro-Bowen ratio instrumentation to compare native, non-contaminated topsoil (A) to both subsoil materials treated by thermal desorption (TD) a 1:1 mixture (by volume) of TD and A (hereafter TDA). The net radiation, latent heat flux, and sensible heat flux were all consistently similar among the three treatments throughout 24 d of data collection before the beginning of the growing season. However, the soil heat flux in TD was much higher than both A (200%) and TDA (150%). This discrepancy was likely caused by a soil crust layer that formed on the TD and increased thermal conductivity at the soil surface. Despite the difference in soil heat flux, the proportion of energy allotted to the latent and sensible heat fluxes were similar among the treatments. Nonetheless, cumulative evaporative losses over 24 d for all treatments calculated using the latent heat flux were all within 5 mm of one another. Thus, the magnitude of difference in soil heat flux was not large enough to alter evaporative losses calculated from the latent heat flux. Overall, these findings suggest the surface energy balance in thermal desorption-treated soils is similar to that of the native topsoil, but that using a mixture of treated soils with native topsoil may better match pre-disturbance conditions.

Introduction

Agricultural soils that are contaminated by petroleum hydrocarbons (PHCs) often require remediation before they are capable of being returned to pre-disturbance levels of productivity. Generally, remediation projects aim to reduce PHC concentrations, whereas reclamation projects take further action to improve conditions for agricultural production. However, remediation methods often adversely affect the ability of soils to function (O’Brien et al., 2017a). Thus, quantifying the effects of remediation on soil characteristics is vital in achieving long-term success in reclamation projects.

One method of PHC remediation is ex situ thermal desorption, wherein contaminated soils are excavated and heated, typically between 250 °C and 550 °C (Troxler et al., 1993; Vidonish et al., 2016), to separate PHCs from the soils via volatilization. The volatilized contaminants are transferred to a thermal oxidizer where they are combusted, and the treated soils are available for reuse. While thermal desorption is a fast, reliable method to reduce PHC concentrations, it does affect many soil properties. Following heating, soils may have altered biological communities (Cebron et al., 2011), increased soil pH (Sierra et al., 2016), reduced cation exchange capacity (Ritter et al., 2017), decreased soil organic matter (SOM), and increased saturated hydraulic conductivity (O'Brien et al., 2016); all of these consequences may affect the viability of thermal desorption-treated soils for use in agronomic systems.

Several options are available to reclaim these excavated, treated soils. First, topsoil may be applied to the area, but this method may not be logistically or economically feasible in many circumstances. Further, importing soil ignores one of the benefits of using thermal desorption, which is the ability to reuse treated soil. Second, the treated soil may be replaced in the excavation. This practice replaces soil that has many altered properties compared to pre-disturbance conditions, so the reclamation process may be very slow and difficult. Finally, the treated soil may be mixed or amended before being replaced. This mixing can reintroduce biological communities and add SOM to the soil, which is associated with many soil physical, chemical, and biological processes. Mixing various disturbed soils with topsoil has been used in a variety of ecosystems to address the characteristics of the disturbed material.

While monitoring changes to individual parameters following TD-treatment is important, evaluating complex, dynamic processes may be more valuable in determining the suitability of these soils for agricultural production. One such process is the partitioning of energy at the soil surface, i.e., the surface energy balance (SEB). The SEB is typically described by four components: i) net radiation (Rn), ii) soil heat flux (G), iii) latent heat flux (λE), and iv) sensible heat flux (H). Often, the SEB is studied in agricultural systems to measure (or estimate) evapotranspiration by quantifying λE (Sauer et al., 1998; Zeggaf et al., 2008; Holland et al., 2013; Kool et al., 2014), effectively closing the water balance. Research examining the SEB has focused on use of different crops (Prueger et al., 1998), different ecosystems (Scarlett et al., 2017), changes between plant canopy and soil surface (Ham et al., 1991), irrigation (Mukherjee et al., 2012), and temporal changes (Odhiambo and Irmak, 2015).

In addition to λE, SEB research is valuable in agricultural systems because it quantifies G, the amount of thermal energy moving through an area of soil over a unit of time (Sauer and Horton, 2005). This flux is critical in describing temporal fluctuations in soil temperature with depth, as well as being important to accurately quantify the other SEB components (de Silans et al., 1997). Changes in G are important in agricultural systems, as they regulate the available energy for biochemical processes of plants (e.g., seed germination; Vigil et al., 1997) and soil microorganisms (e.g., respiration, nutrient cycling; Zak et al., 1999). Thus, SEB has implications for both the water balance and biochemical processes in soil, making it a valuable tool for describing how soils function following soil remediation.

One popular method for partitioning the SEB is the Bowen ratio. For many years, the Bowen ratio has been used extensively in both agricultural and natural environments to effectively describe the relationship between latent and sensible heat fluxes (Irmak et al., 2014). The theory relies upon the assumption that the diffusivity of heat and diffusivity of water vapor are equal across a homogenous surface (Bowen, 1926). Because this technique requires accurate measurement of temperature and water vapor gradients, the scale of measurement is dictated by the sensitivity of instrumentation. Notably, the required fetch of homogeneous surface increases with the scale and height of measurement (Heilman and Brittin, 1989), so more sensitive instruments are required to implement Bowen ratio theory at small spatial scales. Recently, technological advancements have made the implementation of the Bowen ratio theory possible at much smaller scales (Ashktorab et al., 1989; Zeggaf et al., 2008; Holland et al., 2013), allowing for research at the experimental plot level.

This study uses micro-Bowen ratio instrumentation (MBRs) to determine the SEB over research plots comprised of 1) native topsoil, 2) soil that had been remediated using thermal desorption, and 3) a 1:1 mixture (by volume) of topsoil and remediated soil. This research is part of a larger study aimed at assessing viability of using thermally desorbed soil for agricultural production, and these conditions were chosen because they are possible pathways towards reclamation following thermal-desorption treatment. The SEB may be germane to agricultural production because of its relationship to the water balance and soil biochemical process. Therefore, comparing how the SEB is partitioned over these three soil conditions can provide valuable information for remediation or reclamation practitioners considering the use of TD on contaminated soils.

Materials and Methods

Experimental setup

Research was conducted in western North Dakota (USA) adjacent to an active remediation project that was using ex situ thermal desorption to treat agricultural soil contaminated by Bakken crude oil. The project was conducted on large-scale research plots (17 m × 15 m to a depth of 0.9 m) comprised of three materials: (1) native, non-contaminated topsoil (A); (2) thermal desorption-treated subsoil material (TD); and (3) a 1:1 mixture, by volume, of native topsoil and thermal desorption-treated subsoil material (TDA). Full description of soil characteristics and plot construction is given in O'Brien et al. (2017b).

Briefly, the A (Condition 1) was excavated from the site of the research plots, stockpiled for several months, and then used in plot construction. The topsoil was mapped as Williams-Zahl loams (Williams: fine-loamy, mixed, superactive, frigid Typic Argiustolls; Zahl: fine-loamy, mixed, superactive, frigid Typic Calciustolls) (NRCS, 2015). The TD (Condition 2) that had been contaminated by crude oil from a pipeline leak and remediated, which involved passing contaminated soil through a RS 40 Thermal Desorption/Oxidation unit (Nelson Environmental Remediation, Ltd., Edmonton, AB, Canada) at 350 °C for 10 min. The TD was excavated from beneath the A, and materials from all depths up to 15 m below the soil surface were mixed together, so original depths could not be identified. While a majority of TD did not originate from the zone of soil genesis, for ease of reference, this subsurface material is referred to hereafter as "TD soil". The 1:1 mixture (by volume) of A and TD (TDA; Condition 3) was created by alternately adding 0.6 m3 bucket loads of each soil type into a material screener (R155 Screener, McCloskey International, Keene, Ontario). Notably, all plots were uniform in both space and depth within each plot, while treatment differences were identified among all three conditions using multivariate analyses on 26 soil variables (O'Brien et al., 2017b).

During the 2016 growing season, hard red spring wheat (Triticum aestivum L.; variety Barlow) was planted (90 kg ha^{-1}, 30 cm row spacing) and harvested, leaving wheat stubble approximately 10 cm tall. Three soil cores were taken from each plot in the fall of 2016 and divided by depth (see O'Brien et al., 2017b). For samples taken from 0-15 cm depth, particle size distribution was determined using the hydrometer method (Gee and Or, 2002), and soil organic carbon (SOC) was determined as the difference between total carbon and total inorganic carbon found using a Primacs TOC Analyzer (Skalar Analytical B.V.).

In the spring of 2017, a utility terrain vehicle carrying a lawn roller (122 cm width, 61 cm diameter; Ohio Steel Industries, Columbus, OH) filled with water (≈420 kg) was used to flatten the wheat residue and homogenize the soil surfaces. Crop residue counts were then conducted using the line-transect method (Laflen et al., 1981). A 15 m tape measure was laid out across the plot oriented 45 degrees in relation to the rows, and at every 15 cm along the line, presence or absence of litter was recorded to produce a count of litter presence out of 100. Bulk density was determined using aluminum rings (5.2 cm height, 4.8 cm diam) pounded into the ground by a rubber mallet using a custom-built aluminum cap to avoid direct contact between mallet and rings. Rings were centered at 6 cm depth, and dry soil mass was determined after oven drying at 105 °C. Soil color was determined in the field using a Munsell color book (Post et al., 1993). Soil thermal conductivity was determined using a heat pulse probe (KD2 Pro, Decagon Devices, Pullman, WA) on repacked soil samples under both air-dry and fully saturated water contents (Bristow et al., 1994).

Surface energy balance

The surface energy balance at the soil surface can be described as:

$$R_n - G = \lambda E + H \tag{1}$$

where R_n is net radiation, G is soil heat flux, λE is latent heat flux, and H is sensible heat flux (all units in W m^{-2}). In this study, R_n was positive downward to the soil surface, G was positive downward from the soil surface, and λE and H were positive when energy flowed upward away from the soil surface.

The Bowen ratio (β) is the ratio of H to λE (Bowen, 1926) and can be used to partition these components with relation to the total available energy (R_n – G). This ratio can be estimated by quantifying temperature and vapor pressure gradients:

$$\beta = H/\lambda E = [(P_a C_p)/\lambda\varepsilon](\Delta T/\Delta e)(K_h/K_w) \tag{2}$$

where P_a is atmospheric pressure (kPa), C_p is specific heat capacity of air (1004.67 J kg^{-1} °C^{-1}), λ is latent heat of vaporization for water (2.45 MJ kg^{-1}), ε is ratio of molecular weights of air and water (0.622), ΔT is air temperature difference between two heights (°C), Δe is vapor pressure difference between two heights (kPa), K_h is eddy diffusivity for heat (m^2 s^{-1}), and Kw is eddy diffusivity for water vapor (m^2 s^{-1}). Notably, this study assumes that $K_h = K_w$ between the two measurement heights, which has been shown viable in some circumstances (Dyer, 1974; Yaglom, 1977). From Eq. 1 and Eq. 2, λE can be calculated as:

$$\lambda E=(R_n -G)/(1+\beta) \tag{3}$$

and H is then the balance of available energy from Eq. 1.

Micro-Bowen ratio instrumentation measurements

One MBR (described below) was installed on each of the three treatments on day of year (DOY) 103, and each MBR collected data continuously until DOY 148, with occasional downtime for maintenance. Additionally, all instrumentation was removed from the plots on DOY 129 when field peas (Pisum sativum L.) were planted using a Ford 976 Versatile tractor and Flexicoil 5000 air drill, and MBRs were reinstalled on DOY 130. The MBRs were removed on DOY 148 before the field peas emerged, so transpiration was not addressed in this study.

Each MBR was modeled after the design reported in Holland et al. (2013) and included a net radiometer (NR-Lite2, Campbell Scientific, Inc.) that was installed 75 cm above soil surface facing due S to quantify R_n. Soil heat flux was determined using a soil heat flux plate (HFP01, Campbell Scientific, Inc.) installed at 6 cm below the soil surface. Additionally, a water content time domain reflectometer (30 cm length rods; CS616, Campbell Scientific, Inc.), installed horizontally at 6 cm below the soil surface, and a thermocouple (24-gauge type-T), installed 3 cm directly above the HFP01, were included to account for changes in soil energy storage via the combination method (Ochsner et al., 2007; Massman, 1993), where water content, SOM, and bulk density were used to estimate soil heat capacity. Each TDR was calibrated to its respective soil in laboratory conditions to ensure accuracy water content measurements. The HFP01, TDR, and thermocouple were all installed directly beneath the air intakes.

To measure the gradients in temperature and vapor pressure, two air intakes were situated 1 and 11 cm above bare soil surface. Given the size of the research plots, this allowed for ≈100:1 fetch-to-height ratio. Intake tubing (6.2 mm outside diameter, 4.4 mm inside diameter, Synflex ®, Eaton Hydraulics Group, Eden Prairie, MN) extended 15 cm from the main enclosure and was protected by polyvinyl chloride (PVC) piping (25 mm outside diameter, 19 mm inside diameter). Air temperature was measured using thermocouples (30-gauge, type T) attached to the intake tubing. The protective PVC piping was aspirated using fans (Sunon®, Kaohsiung City, Taiwan) to allow for accurate temperature measurement. All intake and exhaust tube openings were filtered using fiberglass wool to prevent debris from accumulating inside the tubing.

Air was pulled through the intake tubing into the main fiberglass enclosure (39 cm × 34 cm × 17 cm; Hoffman, Anoka, Minnesota) via a micro-diaphragm gas-sampling pump (NMP 015, KNF Neuberger, Trenton, New Jersey), where it was transported using flexible PVC laboratory tubing (6 mm outside diameter, 3 mm inside diameter; Tygon ® , Saint-Gobain Performance Plastics, Akron, OH) through a filter (LI-COR Biosciences, Lincoln, Nebraska) and water trap. Air then passed through a solenoid valve (L01 series, Numatics Inc., Novi, Michigan) that alternated flow between lower and upper intakes every 5 min. A flow meter (Cole-Parmer Instrument Co., Vernon Hills, IL) regulated airflow at 1 L min^{-1} before entering a CO2/H2O gas analyzer (LI-840A, LI-COR Biosciences) to quantify water vapor concentration (parts per thousand), which was converted into vapor pressure using atmospheric pressure. After passing through the gas analyzer, air was expelled from the main enclosure via output tubing.

A barometric pressure sensor (CS100, Campbell Scientific, Inc.) installed inside the main enclosure recorded atmospheric pressure every 10 s for the final minute of every hour and averaged for an hourly value. Ambient air temperature and relative humidity were measured using a humidity and temperature probe (HMP60, Vaisala, Helsinki, Finland) installed 40 cm above bare soil surface 2 m from the main enclosure. In addition to the MBR data collection, a weather station was installed adjacent to the experimental plots. This station quantified precipitation (ECRN-100 rain gauge, Decagon Devices) and wind speed and direction (DS-2 sonic anemometer, Decagon, Devices) for the duration of the study.

Data management

The MBRs were controlled by CR10X dataloggers (Campbell Scientific, Inc., Logan, UT) connected to deep cycle batteries (12V 55 Ah) equipped with 100 W solar panels (AcoSolar, Walnut, CA). The loggers collected data every 10 s and averaged values over 5 min intervals, with the first min of every interval excluded. Since the intake to the gas analyzer alternated between upper and lower every 5 min, two intervals (10 min) were required to produce one $\Delta T/\Delta e$ value. Gradients were averaged over 30-min periods (6 intervals) before calculating β. This study focused on the daytime surface energy balance, so only data collected between 7:00 and 20:00 were analyzed.

At this stage, data were rejected based on three criteria. First, data were rejected when the air pump was not active. The pump was programmed to shut off when relative humidity (RH) surpassed 92% to avoid accumulation of condensation in the instrumentation; the pump did not reactivate until RH dropped below 88%. Second, data were rejected when β approached –1, since this can result in flux values that approach infinity. This condition typically occurs around sunrise and sunset when the direction of the temperature and vapor pressure gradients are changing (Savage et al., 2009). Data were rejected in the interval $-1 - |\varepsilon| < \beta < -1 + |\varepsilon|$, where:

$$\varepsilon=(\delta\Delta e-\gamma\delta\Delta T)/\Delta e \tag{4}$$

In Eq. 4, $\delta\Delta e$ and $\delta\Delta T$ are given by the resolution of the sensors for vapor pressure (0.008 kPa) and temperature (0.11 °C), respectively, γ is the psychometric constant ($P_aC_p/\lambda\varepsilon$, from Eq. 2), and Δe is the difference in vapor pressure at two heights (kPa) (Perez et al., 1999). This interval also corrects for uncertainty when ΔT or Δe are less than the sensitivity of the sensors. Finally, data were rejected if they do not satisfy the sign conventions identified by Perez et al. (1999) as they may provide incorrect direction of fluxes. Namely, when $R_n - G > 0$ and $\Delta e > 0$, then λE and H must be positive; but when $R_n - G > 0$ and $\Delta e < 0$, λE must be negative and H must be positive. Conversely, when $R_n - G < 0$ and $\Delta e < 0$, then λE must be positive and H must be negative; but when $R_n - G < 0$ and $\Delta e > -1$, λE must be negative and H must be positive.

Results and Discussion

The MBRs were in place for 46 days, and all three MBRs collected complete daytime datasets for 36 days. A complete daytime dataset was considered continuous measurement from 7:00 to 20:00, with six data points recorded per hour, and the final analysis included 23 days. Thirteen days of data were not used due to high numbers of rejected data entries, which were caused by high RH values or extreme fluctuations in temperature and water vapor at the surface.

The daily average air temperature, daily average wind speed, and cumulative precipitation for that period are shown in Figure 16. Average air temperatures measured at this study were 4.6 °C in April and 12.9 °C in May, which were consistent with 30-year averages, 6.4 °C and 12.5 °C, respectively, measured

15 km from the research area (NOAA, 2017). Similarly, average wind speed during the 46 days of data collection was approximately 3.5 m s-1, slightly lower than the historical average of 4.6 m s-1 (NDAWN, 2017). Notably, the research area received only 8.5 mm of precipitation during the study period, which is much lower than the 30-year average of 61 mm over second half of April and all of May (NOAA, 2017).

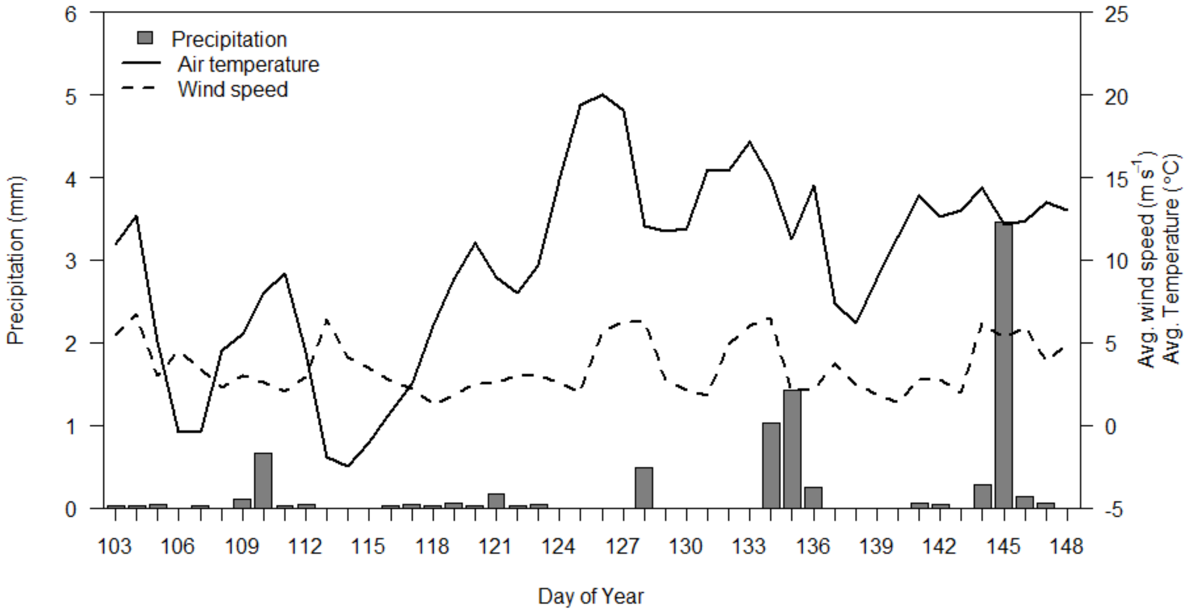

Figure 16. Daily precipitation, average wind speed, and average air temperature during the 46 days the micro-Bowen ratio sensors were installed in western North Dakota. Measurements were taken within 50 m of all research plots.

In addition to climatic variables, soil characteristics for each of the conditions can influence the SEB, and Table 11 shows some of these selected characteristics. The residue cover on the soil surface was similar in the A and TDA, while the TD was slightly lower and much more variable. This residue matches with greater wheat biomass production and yield found in the A and TDA compared to the TD (data not shown). Additionally, the dry soil color of the A was much darker than either other condition, primarily driven by the presence of more organic matter. The greatest difference between the three conditions is the amount of SOC, as the thermal-desorption process typically reduces SOC (O’Brien et al., 206; Sierra et al., 2016), while even mixing of the SOC-rich A into the TD resulted in an intermediate value in the TDA. Despite this difference in SOC, the thermal conductivity of the three soil conditions were similar under both air-dry and saturated conditions (Table 11), likely due to the similarities in mineralogy (O’Brien et al., 2016), particle size distribution, and bulk density.

Table 11. Selected soil properties (with standard error), residue cover, and surface soil color from the three plots on which the micro-Bowen ratio sensors were installed. Particle size distribution and soil organic carbon (SOC) were measured from 0 – 15 cm depth, and bulk density at 6 cm depth. Thermal conductivity was measured in the laboratory using repack soil cores containing soil from 0 – 15 cm depth. A: native, non-contaminated topsoil; TD: contaminated subsurface material treated by ex situ thermal desorption; and TDA: 1:1 mixture, by volume, of A and TDA.

Soil	Particle size distribution			Bulk density	SOC	Residue cover	Soil color		Thermal conductivity	
	Sand	Silt	Clay				Wet	Dry	Dry	Saturated
	---------*g kg*$^{-1}$--------			*kg m*$^{-3}$	*g kg*$^{-1}$	*%*			*W m*$^{-1}$ *K*$^{-1}$	
A	455 (9)	327 (4)	219 (9)	1550 (36)	18 (2)	72 (6)	10YR 3/1	10YR 6/1	0.31	1.36
TDA	451 (3)	321 (4)	228 (5)	1540 (34)	13 (1)	68 (7)	10YR 3/2	2.5Y 5/3	0.28	1.44
TD	434 (7)	326 (6)	239 (4)	1580 (58)	6 (1)	54 (12)	10YR 3/2	2.5Y 6/3	0.28	1.52

Daily fluxes

Figure 17 shows the daytime SEB for the three treatments over two representative days. These days were clear and sunny, with no extreme fluctuations in temperature or vapor pressure throughout the day. The R_n was similar among all of the conditions, and it followed expected diurnal trends, with magnitudes similar to springtime values found in IA (Sauer et al., 1998) and MN (Sharratt, 2002). The R_n was near 0 W m^{-2} at 7:00, peaked around 13:00, and approached 0 W m^{-2} again at 20:00. The component with the greatest differences was G, which was markedly higher in the TD. While G was never greater than 80 W m^{-2} in the A or TDA, it surpassed 150 W m^{-2}midday for both DOY 124 and DOY 125 in TD. Over the course of these two days, trends in H mirrored those in R_n, while λE remained very low. Notably, the fluxes in the TD and TDA at 19:00 and 20:00 fluctuated more than A. This phenomenon is indicative of the change in energy flow at sunset, and it suggests that these changes may occur more rapidly in these soils, possibly due to less residue cover and SOM to regulate changes in energy transfer (Table 11; Horton et al., 1996). These trends are consistent throughout the 23 days included in the analysis, and further discussion of the energy partitioning into each component is included below.

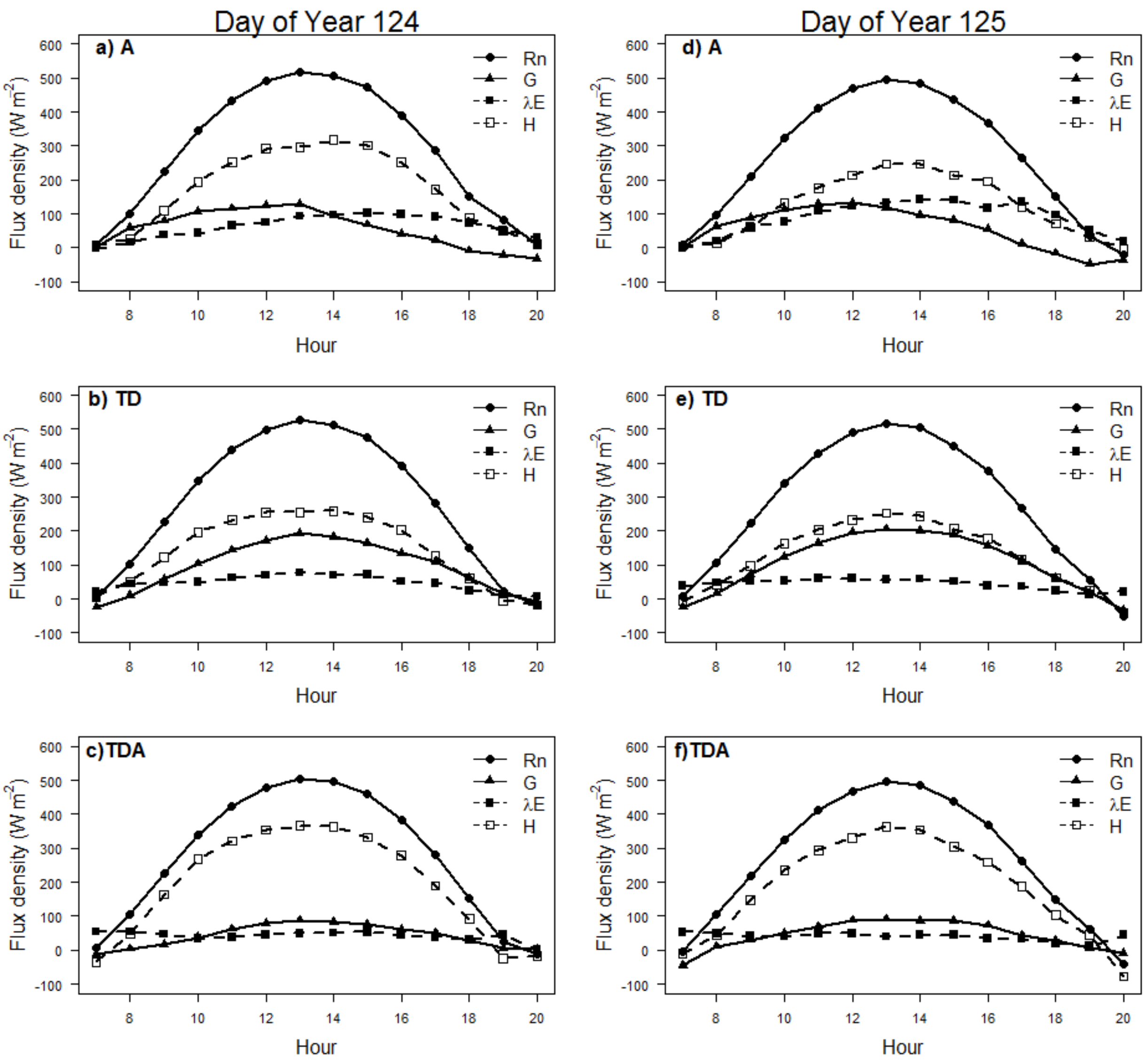

Figure 17. Daytime (7:00 to 20:00) Bowen ratio energy balance for native topsoil (A), soil treated by thermal desorption (TD), and a 1:1 mixture, by volume, of A and TD (TDA). Two representative days are shown, Day of Year 124 (left column, panels a-c) and Day of Year 125 (right column, panels d-f). The components shown are net radiation (R_n), soil heat flux (G), latent heat flux (λE), and sensible heat flux (H).

Net radiation

Daily average R_n values were A: 9.8 MJ m^{-2} d^{-1}; TDA: 10.0 MJ m^{-2} d^{-1}; and TD: 10.1 MJ m^{-2} d^{-1}, which were consistent with values found during springtime in the Northern Great Plains (Frank, 2002; Zvomuya et al., 2008). These values remain similar through the course of the study, and the cumulative Rn for all three conditions were within 2% of one another (Table 12). These similarities in R_n occurred despite the differences in both soil color and residue cover (Table 11). Typically, darker soils are expected to have higher R_n due to lower albedo (Nagler et al., 2000; Post et al., 2000). Similarly, surfaces with more residue cover are expected to have lower R_n, since the reflectivity of the residue is generally higher than the soil surface (Prueger et al., 1998; Nagler et al., 2000; Sharatt, 2002), although this can vary based on composition and depth of residue (Horton et al., 1996). In this study, the differences in soil color and residue cover were likely not extreme enough to cause measureable differences in R_n.

Soil heat flux

Daily average G values were A: 1.7 MJ m^{-2} d^{-1}; TDA: 1.3 MJ m^{-2} d^{-1}; and TD: 2.6 MJ m^{-2} d^{-1}, which resulted in the greatest relative differences among any of the SEB components (Table 13). Two days, DOY 106 and DOY 112, had slightly negative values for all three conditions (Table 12), which was likely due to low R_n values and rapid declines in air temperature. During most of the study, G values were positive, which is expected in dryland soils during the spring while soils are warming (Odhiambo and Irmak, 2015). The mean G values are slightly higher than those found in May on a vegetated reclamation project in Alberta, which ranged from 0.97 – 1.45 MJ m^{-2} d^{-1} (Carey, 2008), and less in Kansas prairie soils that were bare following a springtime prescribed fire (2.3 – 3.6 MJ m^{-2} d^{-1}; Bremer and Ham, 1999).

Differences in G can be caused by variation in incoming thermal energy, thermal conductivity, and soil heat capacity, as G is given by:

$$G=-\lambda(\delta T/\delta z) \tag{5}$$

where λ is the thermal conductivity of the soil (W m^{-1} $°C^{-1}$) and δT/δz is the vertical temperature gradient (°C m^{-1}) in the soil (Sauer and Horton, 2005). Despite similarities in R_n at the soil surface, incoming energy to the soil minerals may have been slightly different among the conditions due to variations in residue cover and SOM. Both residue cover and SOM have higher heat capacity and lower thermal conductivity than soil minerals (Abu-Hamdeh and Reeder, 2000; Horton et al., 1996), which likely intercepted incoming radiation and reduced the amount of thermal energy entering the soil minerals, effectively decreasing G.

Soil thermal conductivity under both air-dry and saturated conditions was similar among all three conditions (Table 11), and they were roughly the same as other reported values for loams with similar bulk density and water contents (Lu et al., 2014). Similarities in the mineralogy, particle size distribution, bulk density, and water content likely overwhelm the decrease in thermal conductivity that normally accompanies soils with higher SOM (Abu-Hamdeh and Reeder, 2000). Further, both the thermal conductivity and soil heat capacity are driven by water content, which is shown in Figure 18. Notably, the probe used to measure water content in this study has an accuracy of 2.5% volumetric water content, and the probe-probe variation can be between 0.5% and 1.5% (Campbell Scientific, 2016). Thus, the volumetric water contents are relatively similar between the three conditions, which also contributes to similarities in soil temperature (Figure 18).

Table 12. Daily totals for net radiation (Rn), soil heat flux (G), sensible heat flux (H), and latent heat flux (λE), respectively, for native topsoil (A), soil treated by thermal desorption (TD), and a 1:1 mixture, by volume, of A and TD (TDA). For 23 days, daytime (7:00 – 20:00) totals (MJ m^{-2}) of each component were calculated using micro-Bowen ratio instrumentation.

Day of Year	**Rn**			**G**			**H**			**λE**		
	A	TDA	TD	A	TDA	TD	A	TDA	TD	A	TDA	TD
104	11.6	11.0	11.3	1.28	1.12	2.81	9.02	9.26	6.33	1.26	0.66	2.12
105	4.31	3.28	4.02	0.75	-0.04	0.33	2.56	1.61	2.03	1.00	1.70	1.66
106	5.24	5.33	5.22	-0.18	-0.50	-0.56	4.50	4.50	4.57	0.92	1.33	1.21
108	4.59	4.76	4.83	0.93	0.65	1.77	3.05	3.77	2.66	0.61	0.33	0.40
109	5.4	5.42	5.70	1.26	0.71	1.80	2.94	4.16	2.61	1.21	0.56	1.29
110	11.2	11.5	11.2	1.55	1.32	2.98	4.96	5.73	4.60	4.67	4.49	3.59
111	12.4	12.3	12.3	2.44	1.83	4.01	6.26	8.88	5.70	3.70	1.59	2.60
112	3.46	3.71	3.76	-0.03	-0.08	-0.08	3.62	3.18	3.76	-0.13	0.60	0.09
118	12.9	13.0	13.3	2.52	1.87	4.75	7.81	9.47	6.63	2.61	1.63	1.88
119	11.7	11.8	12.1	2.09	1.69	3.78	7.54	8.81	6.22	2.08	1.29	2.05
120	13.6	13.1	13.5	2.22	1.67	3.75	8.64	9.64	7.64	2.77	1.75	2.16
121	7	7	6.88	1.01	0.69	1.03	3.39	3.25	3.54	2.61	3.06	2.31
122	6.5	6.71	6.57	0.81	0.54	1.38	4.12	4.51	3.71	1.57	1.66	1.48
123	11.6	11.6	11.6	1.85	1.14	2.95	7.94	9.12	7.37	1.84	1.38	1.27
124	14.5	13.9	14.3	2.82	2.10	4.75	8.53	9.72	7.15	3.16	2.12	2.37
125	13.5	13.5	13.9	2.84	2.19	5.26	6.20	9.30	6.42	4.41	1.99	2.23
126	13.4	13.2	13.8	2.03	1.46	3.48	5.38	9.55	4.84	6.01	2.21	5.51
127	10.7	10.1	10.7	1.74	1.15	2.60	5.94	7.30	4.84	3.01	1.67	3.30
141	14.9	15.2	15.3	3.40	3.38	4.77	8.44	8.56	7.36	3.06	3.23	3.13
145	12.3	12.2	12.1	1.19	0.88	1.08	4.24	3.11	4.42	6.87	8.21	6.54
146	9.39	9.46	9.35	1.45	1.49	1.89	5.70	6.66	5.79	2.24	1.32	1.67
147	12.0	12.3	11.7	2.58	2.37	3.02	5.83	6.81	5.95	3.55	3.10	2.67
148	13.2	14.1	14.0	2.07	2.06	2.82	8.36	8.13	8.33	2.76	3.89	2.83
Totals	**235.3**	**234.5**	**237.2**	**38.6**	**29.7**	**60.4**	**135**	**155**	**122**	**61.8**	**49.8**	**54.4**

Despite the similarities in most of the factors that contribute to G among all three conditions, the G in the TD plot was consistently higher than the A or TDA throughout the course of the study, especially on days with high R_n. While some of the differences in G may be explained by natural variation, some effect of the conditions may also have contributed to changes in G. One possible explanation may be the formation of a surface crust. Crusting can occur under many circumstances, but it has often been associated with rainfall impact on soils with low SOM and low aggregate stability (Ramos et al., 2003; Assouline, 2004; Lado et al., 2004). Since thermal desorption-treatment reduces both SOM and aggregate stability (O'Brien et al., 2016), the TD plots were highly susceptible to crust formation. The crust layer on the TD plots likely increased thermal conductivity at the soil surface because it has a higher bulk density than the rest of the profile (Abu-Hamdeh and Reeder, 2000). Since sampling in this study occurred at 6 cm, the increased bulk density of the crust layer was not identified in those measurements.

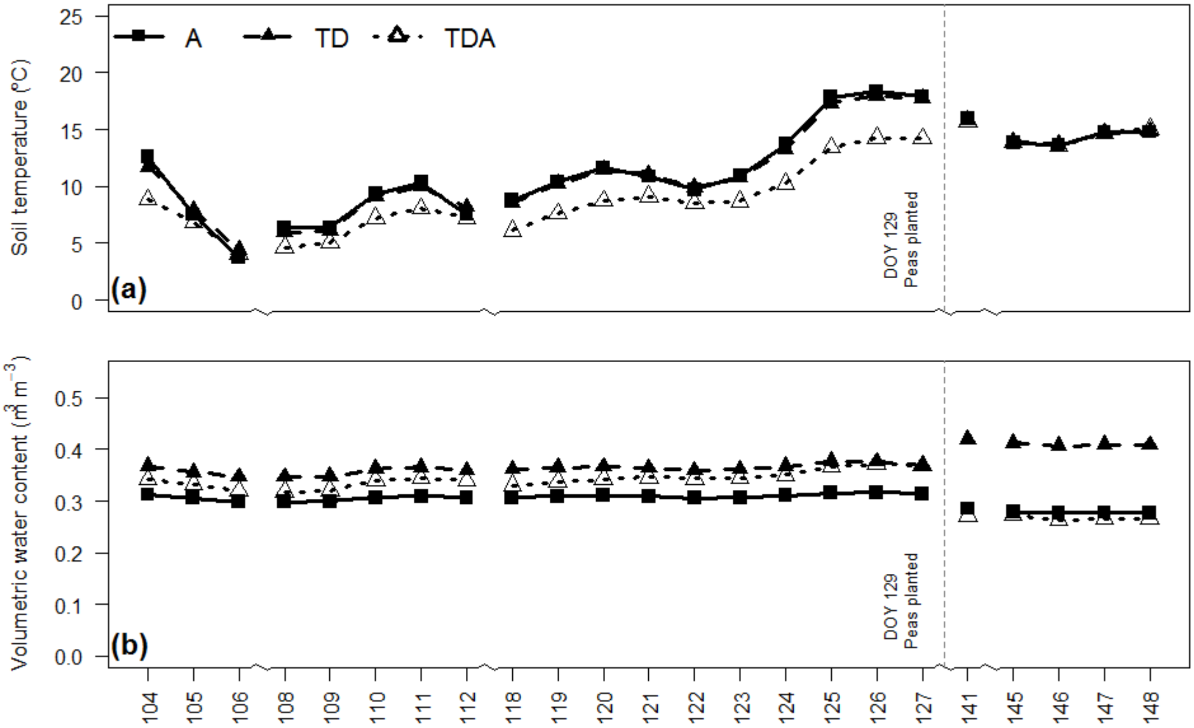

Figure 18. Daily averages of soil temperature at 3 cm below surface (a) and soil volumetric water content at 6 cm below surface (b) over the course of the study for native topsoil (A), soil treated by thermal desorption (TD), and a 1:1 mixture, by volume, of A and TD (TDA). Only the 23 days with full datasets are shown, and discontinuous series of days are signified by breaks in the x-axis, as well as breaks in the trend lines. Single days of data are represented by points only.

Sensible and latent heat fluxes

The average daily H values in the TDA (6.8 MJ m^{-2} d^{-1}) are noticeably higher than the A (5.9 MJ m^{-2} d^{-1}) and TD (5.6 MJ m^{-2} d^{-1}). Since the TDA is a mixture of the TD and the A but is not an intermediate value between the two, this relationship of these three conditions suggests that the differences identified in this study are more likely the result of natural variability rather than differences associated with the reclamation condition. Further, although the absolute magnitude of the differences in

Table 13. Daily ratios soil heat flux to net radiation (G/R_n), as well as sensible heat flux (H) and latent heat flux (λE) to available energy (R_n-G), respectively, for native topsoil (A), soil treated by thermal desorption (TD), and a 1:1 mixture, by volume, of A and TD (TDA). For 23 days, ratios were calculated from daytime (7:00 – 20:00) totals of each component calculated using micro-Bowen ratio instrumentation.

Day of Year	**G/R_n**			**$H/(R_n-G)$**			**$\lambda E/(R_n-G)$**		
	A	TDA	TD	A	TDA	TD	A	TDA	TD
104	0.11	0.1	0.25	0.88	0.93	0.75	0.12	0.07	0.25
105	0.17	-0.01	0.08	0.72	0.49	0.55	0.28	0.51	0.45
106	-0.03	-0.09	-0.11	0.83	0.77	0.79	0.17	0.23	0.21
108	0.2	0.14	0.37	0.83	0.92	0.87	0.17	0.08	0.13
109	0.23	0.13	0.32	0.71	0.88	0.67	0.29	0.12	0.33
110	0.14	0.11	0.27	0.52	0.56	0.56	0.48	0.44	0.44
111	0.2	0.15	0.33	0.63	0.85	0.69	0.37	0.15	0.31
112	-0.01	-0.02	-0.02	1.04	0.84	0.98	-0.04	0.16	0.02
118	0.2	0.14	0.36	0.75	0.85	0.78	0.25	0.15	0.22
119	0.18	0.14	0.31	0.78	0.87	0.75	0.22	0.13	0.25
120	0.16	0.13	0.28	0.76	0.85	0.78	0.24	0.15	0.22
121	0.14	0.1	0.15	0.57	0.51	0.6	0.43	0.49	0.4
122	0.12	0.08	0.21	0.72	0.73	0.71	0.28	0.27	0.29
123	0.16	0.1	0.25	0.81	0.87	0.85	0.19	0.13	0.15
124	0.19	0.15	0.33	0.73	0.82	0.75	0.27	0.18	0.25
125	0.21	0.16	0.38	0.58	0.82	0.74	0.42	0.18	0.26
126	0.15	0.11	0.25	0.47	0.81	0.47	0.53	0.19	0.53
127	0.16	0.11	0.24	0.66	0.81	0.59	0.34	0.19	0.41
141	0.23	0.22	0.31	0.73	0.73	0.7	0.27	0.27	0.3
145	0.1	0.07	0.09	0.38	0.27	0.4	0.62	0.73	0.6
146	0.15	0.16	0.2	0.72	0.84	0.78	0.28	0.16	0.22
147	0.22	0.19	0.26	0.62	0.69	0.69	0.38	0.31	0.31
148	0.16	0.15	0.2	0.75	0.68	0.75	0.25	0.32	0.25
Daily averages	**0.15**	**0.11**	**0.23**	**0.70**	**0.76**	**0.70**	**0.30**	**0.24**	**0.30**

H are higher than in G, the relative differences among the three conditions are much higher for G than H (Table 13, Figure 19), which indicates that the increased G may not be solely the result of natural variability.

H is calculated as a residual from the λE, so the daily and cumulative trends of H and λE inversely mirror one another. Daily average λE values were A: 2.8 MJ m^{-2} d^{-1}; TDA: MJ m^{-2} d^{-1}; and TD: 2.5 MJ m^{-2} d^{-1}. These values were much lower than those found in late spring over vegetated reclaimed soils in Alberta (3.5 – 7.2 MJ m^{-2} d^{-1}; Carey, 2008) and those under burned and unburned prairie soils in Kansas in spring (4.5 – 13.5 MJ m^{-2} d^{-1}; Bremer and Ham, 1999), although comparison of these values can be difficult because λE can be dependent on soil water content. Namely, less energy is partitioned to λE when less water in the soil is available to evaporate at the soil surface (i.e., lower λE when evaporation shifts from stage 1 evaporation at the soil surface to stage 2 evaporation in the subsurface) (Lehmann et al., 2008; Shokri and Or, 2011). Despite lower than average precipitation, water contents remained high (e.g., 0.30 – 0.37 cm^3 cm^{-3}) throughout the duration of the study, which was primarily from the slow wetting of spring snowmelt, so water was available at the soil surface throughout the study. The lower λE values in this study compared to other studies are likely because they did not include any transpiration from vegetation, which can dramatically increase λE.

The cumulative λE (Table 12) can be used to calculate evaporation. This aspect of reclamation is vital in western North Dakota, since increased evaporative losses could make the land unsuitable for agriculture. Over the daytime period of these 23 days, evaporation was highest in the A (27 mm) and lowest in the TDA (22 mm), with TD evaporation calculated at 25 mm. Calculating evaporation from this 14 h period is not complete measure of evaporative loss, as a significant portion of evaporation can occur overnight (Ham et al., 1991, Malek, 1992). However, nighttime evaporation patterns between conditions would not be expected to differ drastically from those patterns observed during the daytime.

Implications for Soil Reclamation

In western North Dakota, yearly precipitation is low (average less than 35 cm) and the growing season is short (about 100 days), so soil water and temperature dynamics are crucial in agricultural production. Any soil disturbance, remediation, or reclamation activities that alters dynamic soil processes associated with water and energy balances could have long-lasting implications for the soil production

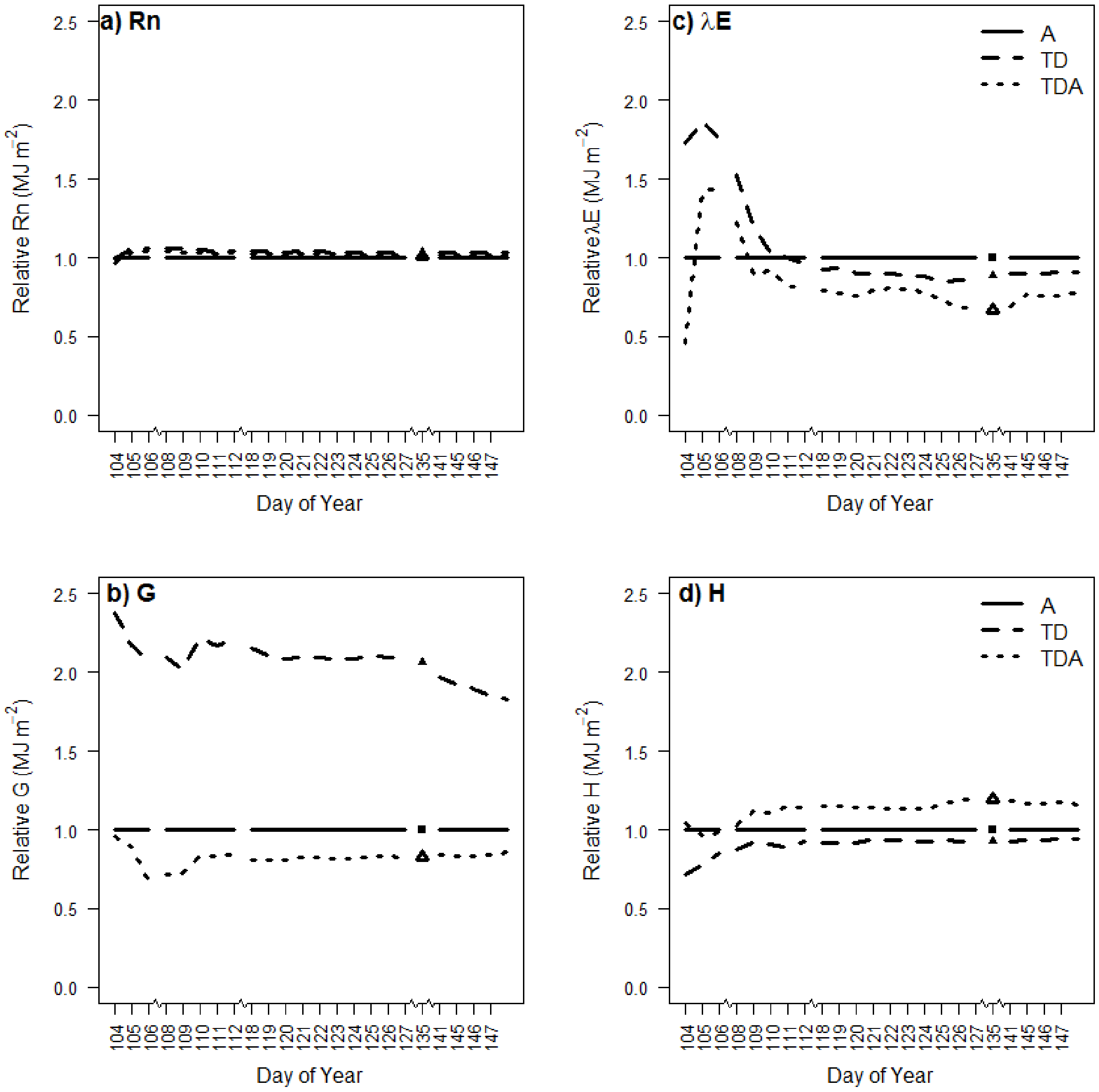

Figure 19. Relative daily values of net radiation (R_n; panel a), soil heat flux (G; panel b), latent heat flux (λE; panel c), and sensible heat flux (H; panel d). Daily values for native topsoil (A) are considered the standard against which relative values for soils treated by thermal desorption (TD) and a 1:1 mixture, by volume of TD and A (TDA) are shown. Only the 23 days with full datasets are shown, and discontinuous series of days are signified by breaks in the x-axis, as well as breaks in the trend lines. Single days of data are represented by points only.

potentials. Quantifying the energy balance over remediated or reclaimed soils can offer useful information for future soil management. However, given the variability of soils in space, with depth, and in time, no standard for an appropriate ‘reclaimed SEB’ exists.

This research utilizes native, non-contaminated topsoil as a benchmark against which to measure the SEB on remediated and mixed soils. Figure 19 shows the daily values for each of the SEB components for both TD and TDA plotted relative to A. Notably, R_n values are nearly identical for all three conditions throughout the study. λE and H values both fluctuate above and below the A values for both TD and TDA, suggesting that daily trends are the result of natural variability. Finally, G values in the TDA fluctuate near the A, but TD values are slightly higher for most days of the study. Although the G was increased in TD, the overall soil temperatures in the root zone were not drastically different from A or TDA. Accordingly, the magnitude of practical effect of the elevated G is comparatively low, especially since less than a quarter of Rn is apportioned to it (Table 13). More relevant to management practices is the relationship of evaporation, as measured by LE, between the three conditions. This research indicates that evaporation was not affected by thermal desorption-treatment at this location, as the difference in total evaporation among the TD, TDA, and A was only 5 mm over 23 days. Thus, increased evaporative losses may not be a primary concern on reclamation projects using thermal desorption-treated soil with similar texture to pre-treated soils.

Conclusions

This study compared the SEB of native topsoil to soils remediated using thermal desorption and a mixture of topsoil and remediated soil. The SEB was quantified using MBRs installed at experimental research plots adjacent to an active oil spill remediation site. All components of the SEB in A and TDA were similar throughout the study, with only minor fluctuations indicative of natural variability. In the TD, R_n, λE, and H were all relatively similar to the A and TDA, but G was slightly elevated. This increase in G is likely the result of reduced residue cover and SOM, coupled with the formation of a surface crust due to reduced aggregate stability. Nonetheless, the soil temperature dynamics and evaporative losses were similar between TD, A, and TDA throughout the duration of the study. This research indicates that SEB over soils from this remediation site treated by thermal desorption are similar enough to A to form a physical environment capable of producing many agricultural crops. However, if the goal of a reclamation project is to mimic as closely as possible pre-disturbance conditions, utilizing the mixture, TDA, may be the best path to success, when sufficient topsoil is not available.

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CHAPTER 6. OVERALL CONCLUSIONS

This research aimed to answer two fundamental questions about soil that had been treated using ex situ thermal desorption: 1) can these soils be used for agricultural production? and 2) how does that production compare to native, non-contaminated, non-treated topsoil? The findings suggest that, in short, these soils can be used in agricultural production, but the quantity and quality of crop yield would likely be diminished compared to undisturbed, native topsoil.

From a strictly functional perspective, the TD-treated soils are capable of performing all six of the functions identified in Chapter 1. Laboratory studies identified that physical and hydraulic properties are all within ranges that are found in soils commonly used for agricultural production across North Dakota. The greenhouse study identified that the TD-treated soils are capable of producing a mature, high quality crop under controlled conditions. Further, the complex, dynamic interaction of these soils with climatic variation, as quantified by the surface energy balance, was not meaningfully affected following TD treatment. Therefore, all of this research indicates that TD-treated soils from this site are initially viable for use in agricultural systems.

While this viability meets a definition of soil reclamation (i.e., the return of the soil to a productive land-use), the overall goal of this particular project extends beyond producing a crop for a single growing season. The ideal outcome is for the soils that are replaced in the excavation area to match local, native, non-disturbed soils in productivity, as well as in most soil characteristics. The greenhouse results indicated that TD-treated soils did not match native topsoil in both crop yield and crop quality after one growing season, and the analysis of soil variables showed that the TD-treated soils and native topsoil are dissimilar in many characteristics. Thus, the recovery of crop production capability and soil characteristics will have to occur over time and may require additional management.

For long-term management of these soils, this research identified some areas of concern. Notably, the recovery of soil organic matter in the TD-treated soils to the levels of native topsoil will be very slow, so nutrient dynamics and aggregate formation will both be altered compared to native topsoil. One way to inject more soil organic matter, as well as a native biological community, into the TD-treated soils is to mix them with native topsoil. This mixing produces material that has soil characteristics more similar to native topsoil than the TD-treated soil, so it may decrease the amount of time needed to match productivity and characteristics of the topsoil. This process is expected to increase crop productivity despite the results observed in the greenhouse experiment. The diminished growth in the greenhouse experiment occurred due to recolonization of the microorganism community. After that recolonization and stabilization under field conditions, which should occur rapidly, the crop production potential is expected to be higher than TD-treated soils alone.

Although TD-treated soils may be suitable for agricultural production at this remediation site, these findings may not be broadly applicable in all situations. Several site-specific considerations may be responsible for minimizing the impacts of TD on these soils. First, the characteristics of Bakken crude dictated that soil heating only needed to be applied at 350 °C for 10 min. Extended heating time or temperature would likely have resulted in greater alterations to soil properties, especially soil organic matter. Additionally, the mineralogy and particle size distribution of the soils in this area did not vary significantly with depth, so the TD-treated material had similar texture to native topsoil.

Nonetheless, this research indicates that TD-treatment of contaminated agricultural soil can allow for crop production following remediation. The decision to use TD-treatment to remediate agricultural soil should include consideration of the subsequent reclamation, as TD will alter soil characteristics based on heating time and temperature, as well as the initial properties of the soil. Notably, mixing TD-treated soil with native topsoil may mitigate some of the impacts of TD treatment and enhance the recovery of soil characteristics and crop production potential.