PHOSPHORUS DYNAMICS AND CROP PRODUCTIVITY IN BAKKEN CRUDE-OIL REMEDIATED SOILS

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Title

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MASTER OF SCIENCE

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ABSTRACT

Thermal desorption (TD), a remediation method used to remove hydrocarbons from contaminated soils, may cause changes in soil properties that threaten soil function and plant productivity. The goal of this research is to better understand the effect that TD treatment has on soils intended for agricultural use. A series of soil phosphorus (P) sorption and desorption experiments were conducted on soils before and after TD treatment to determine P availability for plant uptake and risk for run-off. TD-treated soils retained more P, likely due to mineral transformations of Fe- and Al-oxides. In addition, a three-year field study using mixtures of topsoil (A), crude-contaminated soil (SP), and TD-treated soils (TDU) was conducted. Yields were significantly greater in plots that included A in the mixture compared to SP and TDU soils alone. TD-treated soils can be a replacement for topsoil, but the addition of topsoil will reduce the time to successful reclamation.

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GENERAL INTRODUCTION

As the human need and consumption of oil and natural gas products increases worldwide, the rate of exploration and production (E&P) rises. Accidental releases from pipelines, producing wells, and storage tanks during crude-oil E&P processes throughout the United States, and specifically in western North Dakota (ND), have led to distress for landowners that depend on crop and rangeland as their main source of revenue. While ND's landscape is composed of cropland, rangeland, and energy related infrastructure (oil, natural gas and coal), these entities must harmonize to create a functional ecosystem. During the peak of the most recent boom, total spill volume (hydrocarbon, saline, and other fluids) increased drastically from 8,550 barrels in 2001 to above 162,000 barrels in 2013 (EERC, 2014). These infamous events have created a need to utilize many different strategies for soil remediation and reclamation.

To achieve full reclamation of these lands back to pre-spill conditions, choosing a remediation method is the first step followed by surface reclamation, which commonly consists of applying soil amendments, tillage, and seeding proper seed mixes (EERC, 2014; O'Brien et al., 2017a). However, when the intent is to return the once contaminated soils back to productivity, taking a holistic approach by accessing physical, biological, and chemical soil properties that may have been altered during the initial contamination or remediation method is crucial to the success of surface reclamation (Liang et al., 2012). The specific method researched here is known as thermal desorption (TD). Low temperature *ex situ* TD uses heat to volatilize crude-oil associated hydrocarbons from soil materials allowing them to be returned to the original location and used for its intended service (USEPA, 1994; Hamby, 1996). However, when soils are exposed to such heat soil function may be negatively influenced reducing overall vegetation production.

THESIS ORGANIZATION

This thesis consists of three chapters and is organized in a manuscript format. Chapter 1 is a literature review regarding soil nutrient cycling in highly disturbed soils covering soil pH, N, P, and C as well as implications to relieve common issues seen when reclaiming these soils. This review summarizes changes in soil properties that are crucial for upstream and midstream oil and gas companies to understand when disturbing land during oil and gas recovery processes, as it is essential to successful reclamation. Chapter 2 is titled “Phosphorus Sorption and Desorption of Soils Treated by Thermal Desorption” and focuses on the behavior of P and potential motives for these behaviors after soils are treated with thermal remediation methods. The third chapter, “Crop Productivity of Soils Treated by Thermal Desorption,” spotlights the field study related parameters such as yield, soil water, and soil measurements including organic carbon and aggregate stability. This study provides important information regarding the suitability of TD as a remediation method for crude-contaminated soils that are intended for agricultural use.

CHAPTER 1. EFFECTS OF ENERGY RELATED DISTURBANCES ON SOIL NUTRIENT AVAILABILITY: A REVIEW

Introduction

The energy industry benefits millions of people every day by heating our homes and fueling our cars. Six of the seven continents are producers of oil and gas, and have active surface mining operations. With the increasing demand for these resources comes the need for additional infrastructure for exploitation, refining, and transportation of materials (Mason, 2012), inevitably leading to the disturbance of the soil. Disturbance is defined by Pickett and White (1985) as an event that disrupts an ecosystem, community, or population structure and changes respective resources, substrate availability, and/or the physical environment. To distribute these resources and meet the demands of consumers, the installation of pipelines, an increase in surface mining activities, and the creation of well pads are necessary and soil disturbance is largely unavoidable. Even with advanced technologies, such as underground boring for pipeline installations that largely minimizes soil disturbance, it is impossible to completely avoid disturbance as access roads, well pads, and other infrastructure are all required to complete the energy exploration and production process. The disturbances that will be focused on in this review include the removal and replacement of topsoil (A and desirable B horizons) and subsoil (undesirable B and C horizons) materials during pipeline installations, surface mining, and well pad creation.

In short, construction processes consist of first surveying the land and removal of surplus soils. After the project has been completed, soils are replaced and a reclamation process beings (INGAA, 2018). For example, in pipeline installations, topsoil and subsoil are separated and temporarily windrowed alongside of the work area, generally less than 10 m from the original location (Fedkenheuer, 2000). During this activity, the soil alongside the trench is subject to compaction from heavy equipment traffic. Similarly, in surface mining and well pad creation, topsoil, subsoil, and any other soil layers necessary to reach the desired substance to be mined are removed. Topsoil cannot always be placed directly on already mined land, so these soils must be temporarily stockpiled until an area of land is mined out and in need of topsoil and subsoil materials for the restoration process (Strohmayer, 1999; Shrestha and Lal, 2011 Mushia et al., 2016). However, the length of time these soils are stockpiled before replacement is generally much longer as surface mining and well pad stockpiles are known to be idle for several years to decades (Mason et al., 2011; Mushia et al., 2016) compared to the relatively shorter time period of days to weeks in pipelining. The replacement of soil materials is similar across all scenarios as subsoil materials are placed down, and in some cases graded to the original contour, followed by spreading of topsoil across the landscape.

The removal and methods of replacement of topsoils and subsoils will dictate the length of time needed for reclamation and will depend on many factors. First, the natural depth of topsoil is not uniform across a landscape and Figure 1 illustrates how different soil profiles can vary within a catena. Topsoil in this case, is considered “Ap” or “B” material that is acceptable for plant production according to soil color, structure, and preferably containing no calcium carbonates ($CaCO_3$), or “k” horizons. In addition to “k” horizons, other detrimental horizons such as those labeled “x,y,z”, indicating the presence of salts would be considered unsuitable for topsoil. For this review, subsoils include all “B” and “C” materials that are not suitable for topsoil. A majority of soils in the northern Great Plains are derived from calcium-rich parent materials and the close proximity (North America) of numerous studies regarding energy related disturbance suggests the soils develop from similar calcium rich materials. The presence of $CaCO_3$ within Figure 1 is presented by “Bk” and “Btk” horizons. When topsoils and subsoils are stripped and stockpiled, it is crucial to keep the separation between topsoil and the subsoils that can be detrimental to plant productivity such as “B” and “C” horizons that include “k” or “x,y,z” horizons as “soil dilution” or “soil mixing” can occur, which may decrease function of the plant rooting environment.

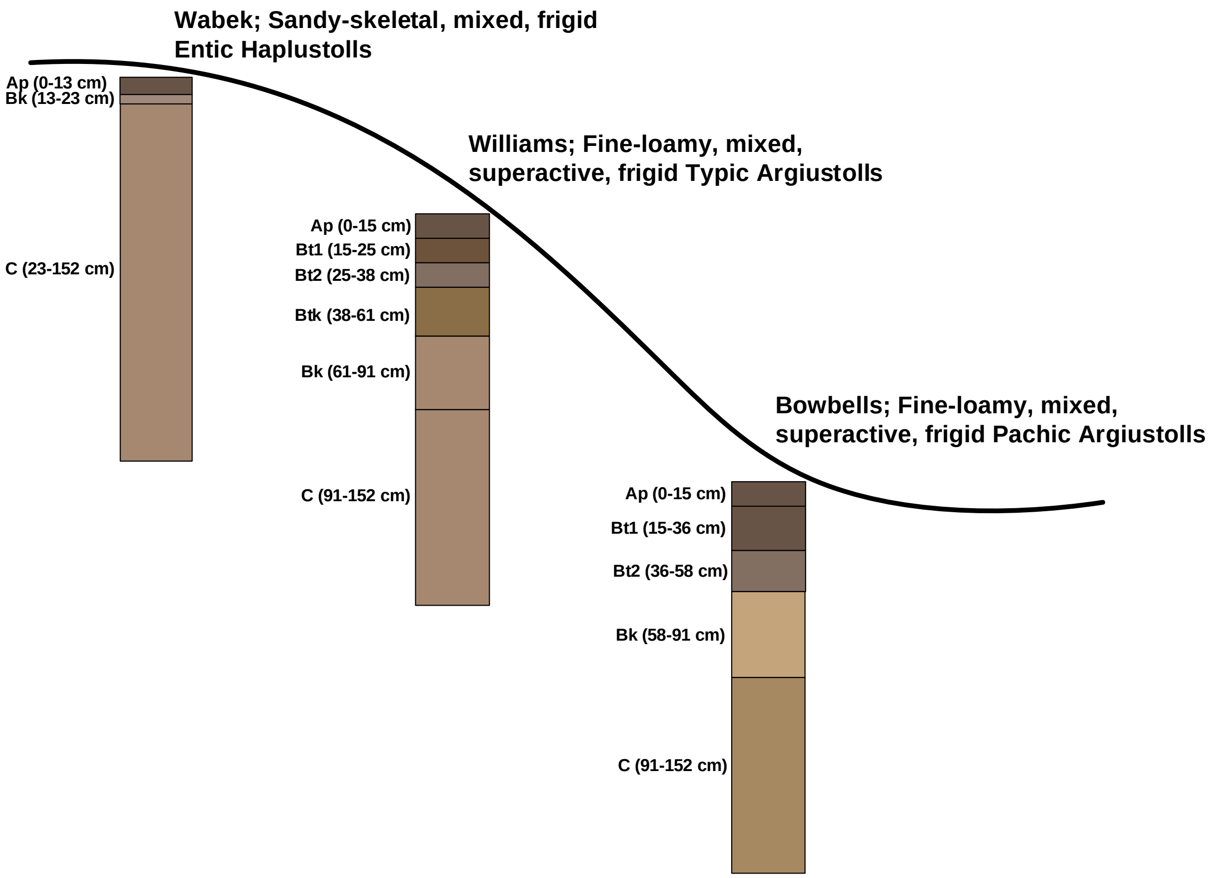

Figure 1. The variation of soil development across a landscape. A and B horizons in absence of k subhorizons are considered suitable for topsoil. Horizons and soil colors are from the official series descriptions (accessed November 6, 2018; https://soilseries.sc.egov.usda.gov/osdname.aspx)

The concept of soil mixing, as it will further be referred to as, has been discussed in several studies regarding reclamation of disturbed soils (De Jong and Button, 1973; Culley et al., 1982; Gasch et al., 2014), and occurs when amounts of topsoil and $CaCO_3$ containing subsoils, or other undesirable subsoil properties, become blended. For example, the introduction of $CaCO_3$ leads to an increase in alkalinity (pH) (Gasch et al., 2014; Shi et al., 2014; Gasch et al., 2016) because, upon dissolution, $CaCO_3$ undergoes a reaction where Ca^{2+} ions separate from the CO_3^{2-} and Ca^{2+} replaces hydrogen (H^+) ions on the soil exchange complex, the controller of pH. Hydrogen then reacts with CO_3 to form carbon dioxide (CO_2) and water (H_2O). By removing the acidity (H^+) from soil solution, the pH is increased (Ketterings et al., 2005). Largely due to the increase in pH, a soil parameter that can dictate the availability of plant nutrients, mixing of topsoils with subsoils has proven to alter chemical and biological properties of the soil as decreases in microbial abundance and shifts in nutrient availability have been reported in response to soil mixing (Allen and Allen, 1980; Gasch et al., 2016).

Secondly, when topsoils and subsoils are stripped during the removal process, often times a specific depth or volume of topsoil is determined to be removed across an entire landscape through the specifications of the project engineer. For example, in the case of road or pipeline construction, kilometer stretches are stripped of the same depth of topsoil. The use of pre-construction surveys is not common for classifying topsoil but more for the suitability of subsoil materials and their ability to support structures such as roads or building foundations. The only concern with topsoil is that a minimal depth requirement be replaced after construction (Personal communication; M. Reker, 2018). However, as depicted in Figure 1, the Wabek series located at the summit position, is likely to contain less acceptable topsoil, 0-13 cm, than that of the Williams and Bowbells series, 0-25 and 0-58 cm (to depth of Bk horizon), respectively. Further, the boundaries between soil horizons is not always linear and can be irregular and wavy (Schoeneberger et al., 2012). Thus, by understanding soil profiles and their development across a landscape, construction practices during the removal process can be tailored to correctly remove topsoil and subsoil separately to prevent soil mixing.

The soil profile configuration during replacement is the first step for successful soil reclamation and is highly dependent on how soil materials are separated and arranged during replacement. Figure 2 shows the initial state of the soil profile (top), similar to that of Figure 1 and the three potential outcomes of how the soil profile may look after various levels of precision during removal and replacement. Outcome 1 represents the ideal soil profile with separation of A, B, and C, horizons. The ideal outcome allows for accumulation of dark, organic matter rich materials at the surface that will likely redevelop soil structure and function faster. Outcome 2 displays the soil profile when A and B horizons are separated to the best of the equipment and operator abilities of using soil color as a main indicator between topsoil and subsoil materials. However, because of variation in soils and irregular boundaries, an operator may do everything correctly but small amounts of carbonates may still be introduced to the surface with the potential to alter soil properties. Outcome 2 has a lighter surface color and a slightly higher pH. Outcome 3 occurs when topsoil and subsoil materials are vastly mixed with each other with minimal effort to properly separate. Not only are great amounts of carbonates introduced into the surface, the massive soil structure and potentially different textures from below horizons can affect a suite of soil properties (i.e. soil pH, nutrient availability, infiltration, etc.) in soil now being used as a medium for plant production, and thus overall soil function may be reduced.

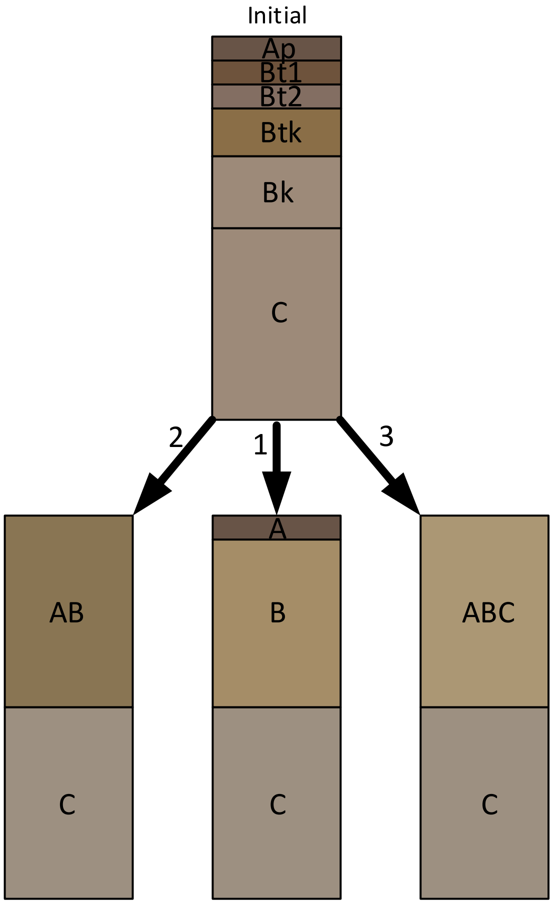

Figure 2. Three potential outcomes dependent on the practices used during soil removal and replacement. The top profile represents the initial, undisturbed soil profile. Outcome 1 represents the ideal soil profile with separation of A, B, and C, horizons; outcome 2 displays the soil profile when A and B horizons are separated to the best of the abilities of equipment and operators; outcome 3 occurs when topsoil and subsoil materials become mixed, largely altering soil properties.

The time to a successful reclamation is a function how well soils are removed and replaced. According to the North Dakota Surface Coal Mining and Reclamation Operations performance standards, the end goal of reclamation for prime farmland is to reach 90% relative productivity of the original condition of the soil (ND Legislative Branch, 2018). Therefore, putting forth more effort to separate topsoil from subsoil on the front end, during preconstruction, and the careful placement of soil during the final stages may allow for a more efficient time to reclamation. Achieving reclamation more efficiently allows for satisfaction by landowners and economic benefits for all parties involved.

Aside from soil mixing, the moment that soils are disturbed from their natural state by earthmoving equipment, physical properties of the soil become altered (Strohmayer, 1999). Though large equipment is used to manage soils in modern agriculture, the equipment being used in these circumstances is exponentially larger in size and weight, therefore incomparable. The depth of soils affected by tillage in agriculture is usually less than 0.15 m, while complete removal and replacement can influence meters of soil. Therefore, disturbances from construction actives such as these cannot be grouped into the same category as agriculture related tillage practices. Physical properties like bulk density have been increased due to heavy equipment traffic and excavation causes disruption of soil aggregates (Ingram et al., 2005; Anderson et al., 2008), both influencing nutrient cycling and microbial activity (Abdul–Kareem and McRae, 1984; Strohmayer, 1999), and overall plant production potentials of these soils (DeFalco et al., 2009; Coiffait-Gombault et al., 2012).

Soil Aggregation and Compaction

Changes in soil physical properties are directly related to the construction process. The movement of soil allows for soil aggregates to be disrupted while heavy equipment traffic increases bulk density and severity of compaction. Soil aggregates play a large role in soil health but, in particular, nutrient cycling and availability. For C and N, previous research illustrates a flush of nutrients following soil disturbance such as with surface-mine reclamation (Beare et al., 1994; Ingram et al., 2005; Wick et. al., 2009). This may be explained by the breakdown of soil aggregates that allows trapped nutrients to enter the available form, but only temporarily. Long term, these nutrients will be released into the atmosphere or relocated via aqueous flow becoming unavailable to plants during the reclamation process. This theory has been explained and is reason for enhanced vegetative growth immediately following topsoil replacement (Wick et al., 2009). Figure 3 illustrates the relative nutrient availability over time influenced by total porosity and bulk density. After disturbance, baseline aggregation and bulk density may both be reduced. After removal and replacement of soil materials, the pore volume increases and creates a “fluffy” soil with a low bulk density, as they are inversely related (Shi et al., 2014). Due to the higher infiltration rates of water, increased availability of O2, and the disruption of aggregates (Wick et al., 2009), nutrient availability during post-soil replacement increases allowing for optimal plant productivity immediately after a disturbance. However, over time, soil pores will begin to subside causing this mineralization process to decrease, thus decreasing the availability of soil nutrients. In addition, subsidence causes increases in bulk density creating the potential for compaction and root-restricting environments.

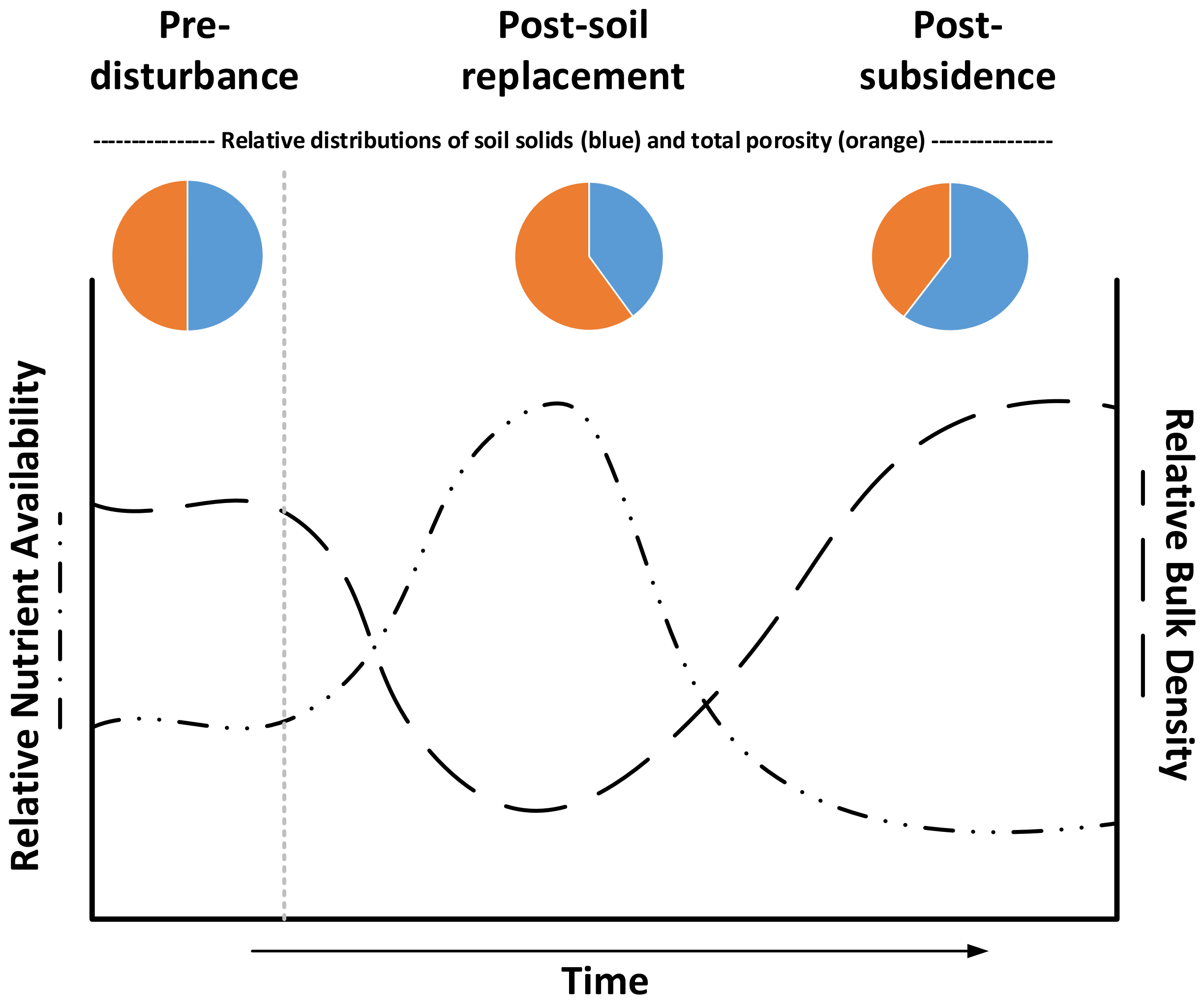

Figure 3. Relative nutrient availability over time influenced by soil solids, total porosity, and bulk density. Pre-disturbance conditions are the reference soil and time of disturbance is noted by the vertical dashed-gray line.

Compaction may occur due to subsidence or from traffic, which can cause an increase in bulk density and decrease in infiltration (Hammermeister et al., 2003; Liu et al., 2017). Furthermore, compaction can alter soil structure, decrease porosity, and overall reduce soil organism abundance and activity (Shrestha and Lal, 2011; Mylliemngap, 2016). The amount of compaction can partially be dictated by the soil water content when construction activities are being done. For example, between 70 and 80%

of compaction occurs during the first pass and any soil type is subject to compaction when soil water content is at or above field capacity (Wolkowski and Lowery, 2008).

Irrespective of how compaction occurs, decreases in crop yields are likely (Culley and Dow, 1988; Shi et al., 2015) due to limited root growth. Also, reduced water infiltration and nutrient uptake by the plant then alters the overall nutrient cycle (Dunker and Barnhisel, 2000; Fedkenheur, 2000). However, soil chemical properties may not be impacted unless they depend on reduction-oxidation pathways.

Soil Water

In arid or semi-arid regions, where plant-water stresses are common, disruption of soil may have positive or negative effects. In a few instances, recently disturbed soils had an increase in soil water (Shukla et al., 2004; Gasch et al., 2016), likely due to increased infiltration. However, after soil settling or subsidence, total porosity decreases, impeding water infiltration. Consequently, establishment of vegetation on disturbed soils with reduced water can be challenging. In addition, the reduction in vegetation may accentuate soil erosion and decrease the potential for soil development, thus decreasing biological activity and nutrient cycling (Wood and Buchanan, 2000; Minnick and Alward, 2012). In short, in arid and semi-arid regions especially, minimizing the severity of compaction in topsoils and subsoils will allow for increased soil water, increased biological activity, and increased potential for plant production.

The soil properties and their interactions affected by the improper removal and replacement of topsoils and subsoils, whether it be because of soil mixing or the unavoidable physical handling of soil, ultimately influence soil function and plant productivity/yield (Figure 4). These disturbances influence a suite of properties (Buto and Kenne 2010; Shale et al, 2010) and by taking a holistic approach and considering all physical, chemical and biological properties and their influence on each other, these disturbances can be better understood and recommendations for improvement can be made to minimize time to successful reclamation.

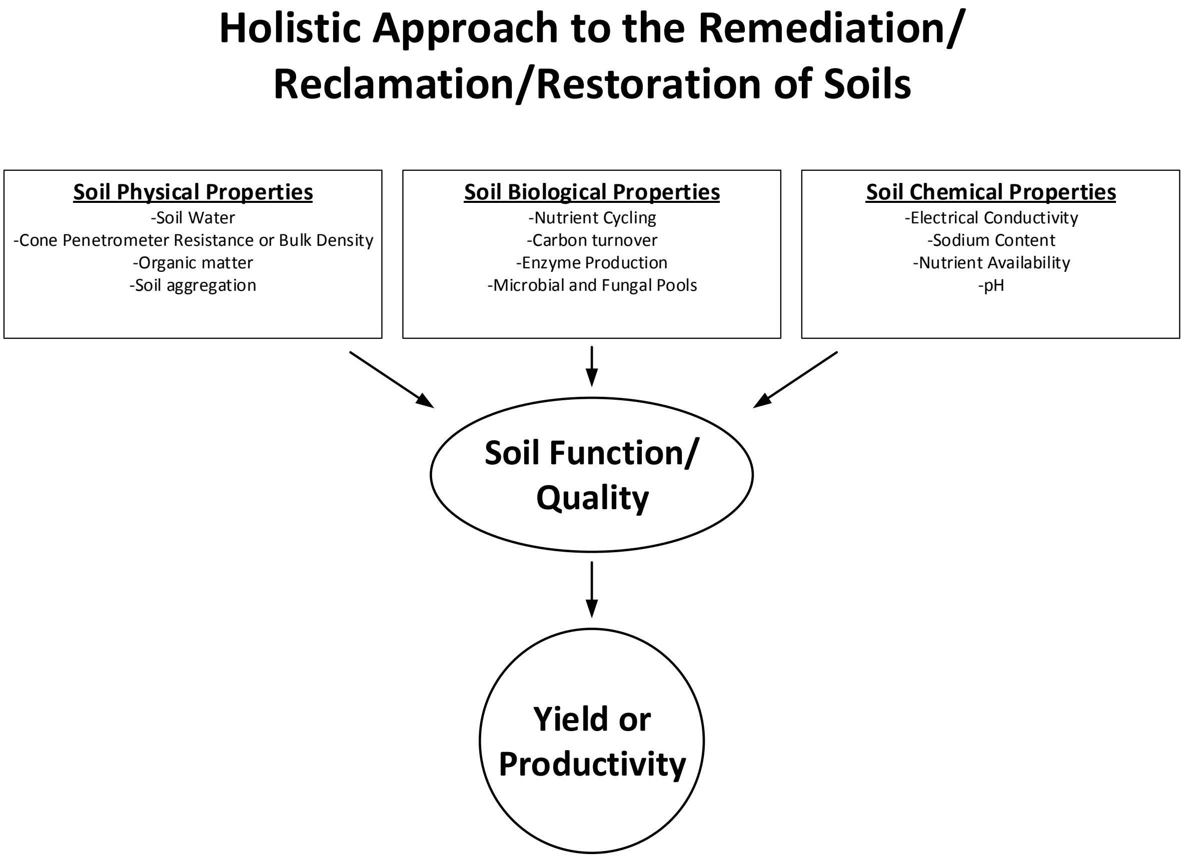

Figure 4. A holistic approach to remediation/reclamation/restoration of soils. Adapted from Barnhisel et al. (1992).

Although the work studied in this thesis pertains to crude-oil releases and the specific remediation method associated with such spills, all disturbances from the energy industry leave lasting effects on supporting ecosystem services, such as nutrient availability, that living organisms depend on for survival (Allred et al., 2015; Tardieu et al., 2015). The amount of agriculture and natural lands impacted by disturbances also have economic impacts, and to ensure economic prosperity as well as quality of life for citizens, investigating the changes within the directly altered soil matrix is the first step. This review summarizes changes in soil properties that are crucial for upstream and midstream oil and gas companies to understand when disturbing land during oil and gas recovery processes. By understanding the changes in nutrient availability and pH, soil handling practices may be improved to reduce the time to successful reclamation. The minimization of soil mixing will ultimately minimize the changes in nutrient availability and pH, making soils more resilient and sustainable in the long term.

While impacts of soil disturbance and reclamation have been reported in the scientific literature, the body of work is sparse, particularly with regards to nutrient availability. The following sections summarize how energy related disturbances are affecting soil fertility related properties in disturbed soils (pipelines, mine lands, well pads). The most commonly researched and most important nutrient pools to vegetative growth are N, phosphorus (P), and C which is not surprising since N and P are the two most essential nutrients for plant production while C is one of the most critical elements to soil function (Corning et al, 2016). Soil pH was also considered because of its influences on nutrient availability. Acquiring a more holistic understanding of nutrient availability in disturbed soils can lead to more educated inferences and recommendations for successful reclamation, irrespective of whether the soil will be used for crop or rangeland production.

Search Methods

Search of Literature

To investigate the effects that energy disturbances have on soil nutrient availability, a review of the literature using Web of Science™, Google Scholar™, and NDSU Libraries databases was conducted. The search included only studies that were peer-reviewed and available in the English language with the exception of studies published in proceedings of the 1992 National Symposium on *Prime Farmland Reclamation* as these studies met the search criteria but are not accessible in an online format. The search was conducted using the terms in Table 1 accompanied by AND “soil chemical properties” “soil nutrients” and/or a specific soil nutrient or property. The search recovered many papers during the first round of searching, but not all discussed the focus parameters. To widen the scope of papers reviewed, the search terms were expanded to more general terms regarding disturbance and the papers were selected based on the main research focus of energy related disturbances. These terms included “soil chemical properties AND disturbance”, “disturbed soil”, and “reclamation” and the “specific parameter desired (pH, N, P, or C)”.

Table 1. Terminology used in literature search.

Topic	**Search Term**
Pipeline installation and burial	Pipeline installation, pipeline burial, pipeline construction, pipeline disturbance
Surface mining†	Surface mining, surface mining replacement, mining soil replacement, coal mining, mine lands
Well pad development	Well pad construction, well site construction, well pad abandonment, well site abandonment, well pad development, well site development

†The topic of surface mining did not include mining of heavy metals.

For the article to be accepted for this review, it needed to discuss the event of an energy related disturbance while additionally evaluating properties such as pH, N, P, and/or C, in a disturbed area with an undisturbed area as a reference or a similar instance where such comparison could be made. Many articles were removed from the review as they assessed reclamation methods by application of fertilizer but articles that discussed amendments for reclamation and those that were located in non-typical areas (wetlands, extreme desert or extreme frigid climates) were removed. Finally, articles that reported at least N, P, C and pH data for soils were chosen, yielding a total of 22 articles for this review. A majority of the articles used in this review were located in North America (Canada n=9; Wyoming n=6; Illinois n=1; Kentucky n=1; Ohio n=1) with the exception of four articles from eastern China (n=4).

Amongst the review articles, the most common soil chemical characteristics and those that are pertinent to successful crop production were pursued; pH, total N (TN), and soil organic carbon (SOC). Additionally, available N (AN), total P (TP), available P (AP) and soil organic matter (SOM) were mentioned and also collected. The most commonly researched and most important nutrient cycles to vegetative growth are those of nitrogen (N), phosphorus (P), and carbon (C). Nitrogen and P are the two most essential nutrients for plant production as well as the infamous nutrients often associated with environmental concerns. Soil N is the most essential nutrient for crop production and is utilized by plants in the ammonia (NH_4^+) and nitrate (NO_3^-) forms (Walworth, 2013; Kruse et al., 2015), while P is the second most limiting and available in soluble phosphate form. Meanwhile, C is one of the most critical elements to soil function (Corning et al, 2016). Soil pH was also considered because of said nutrients contingency on pH. If these nutrients are not present in available forms for plant uptake, deficiencies occur and thus, productivity decreases.

The information gathered from the articles was used to produce a short review on how nutrient pools change after soil disturbance. Data was extracted from each article (soil depths of 0 to 60 cm), organized by parameter, and analyzed based on if the amount of the respected parameter increased or decreased after the disturbance. An increase was marked with a “+”, a decrease with a “-“, and no change with a “0” (Table 2). Interpretation of the specific parameter will affect whether or not the increase or decrease will be positive or negative to the soil’s overall function.

Table 2. List of literature articles included in this review with changes in their respective parameters assessed.

Author	pH	Total N†	Available N	Total P	Available P	SOC	SOM
Pipeline installation burial							
De Jong and Button, 1973	+	-		-			
Culley et al., 1982	+	-		-			
Culley and Dow, 1987	+	-		-	-	-	
Naeth et al., 1987	+					-	-
Landsburg, 1989	+						0
Soon et al., 2000a	+	-				-	
Soon et al., 2000b	+	-	+		-	-	
Gasch et al., 2014	+	0				-	
Shi et al., 2014	+	-	-	-	-		-
Xiao et al., 2014	+	-	-	-	-	-	-
Shi et al., 2015	+	-	-	-	-		-
Gasch et al., 2016	+	-	+			0	
Surface mining and replacement							
Allen and Allen, 1980	+	-			-		
Indorante and Boast, 1981	0					-	
Visser et al., 1983	-	-		-			
Semalulu and Barnhisel, 1992				-	-		
Shukla et al., 2004	+	-				-	
Shrestha and Lal, 2011	+	-				-	
Liu et al., 2017	+	-	-	-	+		-
Well site development							
Hammermeister et al., 2003	+	-				-	
Anderson et al., 2008	+	-				-	
Mason et al., 2011			-			-	

†Symbols -, +, and 0 indicates a decrease, an increase, and no change, respectively in each soil parameter.

Effects of Soil Disturbances on Soil Properties

Soil pH

The most obvious change in soil chemical dynamics was the increase in soil pH (Fig 5) as it was measured in 20 studies and an increase after disturbance was observed in 90% of the time (Table 2). An increase in soil pH can affect the growth of plants as a majority of plants prefer pH values near 6.5 (Ketterings et al., 2005). pH is largely chemical driven, and can inhibit plants' ability to uptake not only macro, but also micronutrients. The increases in pH found within this review generally are not a threat to plant productivity with the average increase being around 0.5 units. However, in Soon et al (2000b), soil pH started at 5.5 and increased to 7.5 after disturbance. Similarly, soils that possessed pH values of near 6.5 did have increases in pH to near 8.0, which is higher than desirable for most plants and alters the chemistry of the soil having a cascade effect on other soil properties (Naeth et al., 1987). This increase in pH is attributed to the introduction of $CaCO_3$ from lower in the profile and primarily occurs as a result of soil mixing.

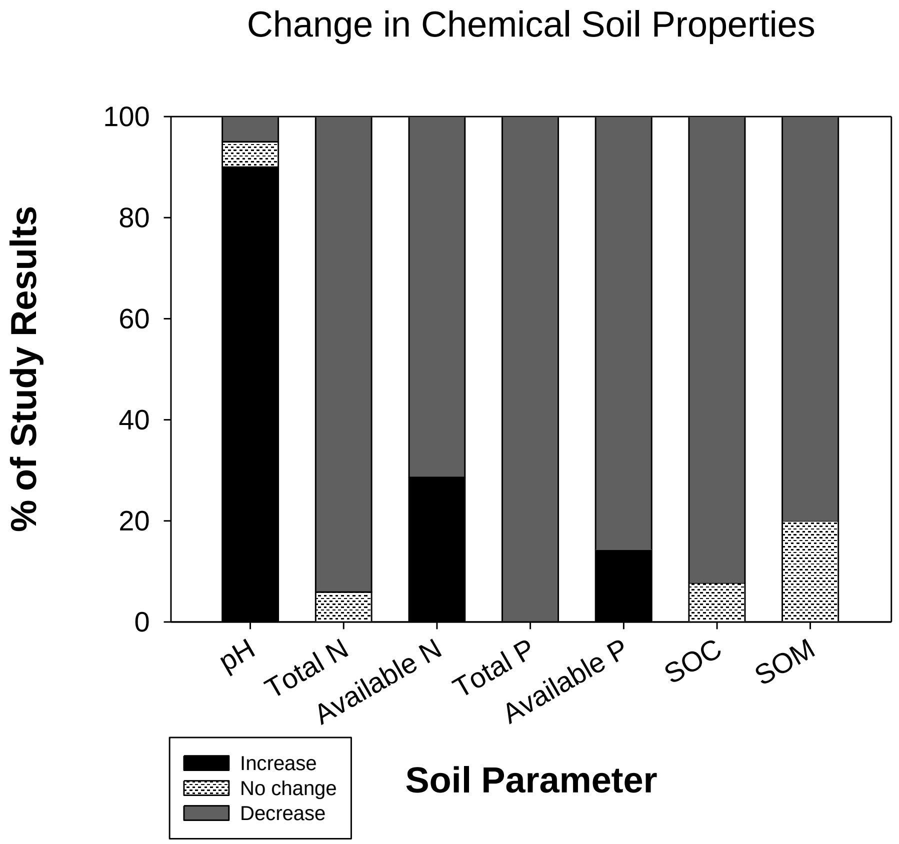

Figure 5. Changes in N, P, and C nutrient pools and soil pH. Number of articles per parameter: Total N (n=17), Available N (n=7), Total P (n=9), Available P (n=8), SOC; soil organic carbon (n=13), SOM; soil organic matter (n=5), and pH (n=20).

Soil Nitrogen

Total N decreased in a majority (94%, n=17) of the articles, but available N (n=7) was more variable with 28.6% of articles showing increases (Table 2, Fig 5). For example, Shi et al (2014) documented a 20% total N decrease relative to an undisturbed value of 1.02 g kg^{-1} after pipeline installation. The instances where increases in available N were documented can be explained by the mixing of topsoil and subsoil materials that accelerates mineralization of N compounds as they are exposed to aeration and temperature (Wick et al., 2009). Mineralization increases with disturbance and is greater in topsoil (Mason et al., 2011). The handling of the soil causes aggregates to break up and release mineralized nutrients that were formerly protected by aggregate structure (Wick et al., 2009). Those nutrients then become more readily available for plant uptake and microbial consumption (Visser et al., 1983; Ingram et al., 2005). This N may be immediately available but is often leached or volatilized out of the soil by the time it is placed back for plant production (Soon et al., 2000a), explaining the overall decrease in both N parameters.

Available N showed a more neutral change but negative trend within the studies evaluated in this review. Similar results were found in other studies as available N was lowest in the trench and work areas of pipeline installations and highest in undisturbed areas beyond 20 m from pipelines. Though these responses were variable, it is important to keep in mind that there are cases when soil nutrients become more available after disturbance (Figure 4) because of the release of nutrients from soil aggregates.

Soil Phosphorus

Total P (n=9) decreased in all studies (100%) with available P showing reductions in 86% of the studies (n=8) (Table 2, Fig 5). Soil mixing was evident in the Shi et al. (2014) study where Total P and available P reference values were 0.66 g kg^{-1} and 30.8 mg kg^{-1} in the 0-10 cm depth compared to 0.62 g kg^{-1} and 16.9 mg kg^{-1} in the pipeline piling area, respectively. Another explanation related to soil mixing for the decrease in available P can be due to the creation of calcium phosphate due to the increase in soil pH and $CaCO_3$, which reduces P for plant uptake (Tisdale and Nelson, 1985). Although not a focus of this review, phosphatase activity in the 0-10 cm depth has been proven lower than baseline, pre-disturbance levels (Soon et al., 2000a). This enzyme is key in the conversion of organic P to inorganic P which is directly available for plant uptake (Stevenson and Cole, 1999).

Soil Carbon

Soil organic carbon and SOM both decreased in 92% and 80%, respectively, after disturbance (Fig 5). Soil C is greatly affected by physical disturbance of soil properties as seen in Shrestha and Lal (2011) where a 56-83% decrease in SOC concentrations was seen in the top 15 cm of newly reclaimed surface mine soils. The decrease in SOC is attributed to the depletion of SOM by exposure to oxygen, warmer temperatures, and water, which accelerates mineralization of carbonaceous materials thus decreasing SOC (Stahl et al., 2002). In addition, soil mixing plays a role in the decrease of soil C as increases in pH influence soil SOM and SOC levels (Shrestha and Lal, 2011). Like N, C is occluded in soil aggregates and disturbances cause a release of C into pools where microbes can mineralize it. Increases in respiration are reported in soils with disturbance because of organic matter coming into contact with microbes, creating a substrate for biomass production (Ingram et al., 2005; Zakharova et al., 2014). This leads to C and N turnover (Killham et al., 1993) and it is also suggested that soil water, a function of porosity and infiltration, during the stage of construction or reclamation can affect the cycling and turnover rate of C (Gasch et al., 2014).

Applied Management/Implications

Soil properties will likely be altered after disturbances, and soil mixing can account for most of the changes in disturbed soil properties. To ameliorate soil mixing and the related consequences (i.e. pH increase), there are a few potential strategies to adopt. First, there are common misunderstandings of what topsoil is and by educating heavy equipment operators on simple soil properties such as soil color, texture, organic matter, and the presence of calcium carbonates could improve precision when stripping topsoil and subsoil. For example, Fedkenheur (2000) explains the many definitions of topsoil from, “the layer of soil moved in cultivation,” to “the fertile soil material used to topdress gardens and lawns,” which these definitions do not disclose the above-mentioned soil properties. With increased knowledge about these properties, operators can better identify topsoil from subsoil rather than a set depth across the whole landscape, as soils vary spatially. When replacing the soil after disturbances like pipeline installations and surface mining, the process must be vigilant. Results from within the literature assumes that much of the soil mixing occurs when the soils are backfilled into the trench. By carefully placing subsoil first followed by topsoil, with little mixing as possible, soil property change can be minimized (Indorante and Boast, 1981; Landsburg, 1989), which will allow for the process of soil reclamation to proceed at a faster pace.

In the event that soil pH does increase, it should be monitored yearly after the disturbance with the likeliness that $CaCO_3$ will be leached down the profile if there is an adequate amount of infiltrating water, returning pH values back to normal 3-5 years after soil mixing occurs (Soon et al., 2000b; Gasch et al., 2014). The depth to saline or sodic soils is an important factor when determining topsoil depth as soil mixing may occur, because unlike soil pH that has shown to regulate itself after a number of years, the introduction of salts into soils can increase the time to successful reclamation.

The unavoidable portion of soil removal and replacement is the physical disturbance of soil aggregates. Minimizing the amount of times soil is handled and traveled upon is one way to lessen the destruction of soil aggregates that are essential for soil structure and contain soil nutrients. Compaction is of large concern as soil aggregates are broken down and pore space is reduced (Slowinski-Jurkiewicz an d Domzal, 1988). To ameliorate high bulk densities, deep ripping or tillage may be used (Voorhees, 1983). One deep tillage pass before the first seeding event is likely sufficient to shatter the compaction layer. After this, established root systems will improve soil structure, additional tillage passes will only increase deep compaction layers.

In cropping systems, the modification in nutrient availability due to soil mixing may not be of major concern because fertilization can be implicated. However, establishment of certain plant species will still remain a challenge. Also, weed pressure may become troublesome in cropping systems but especially in sites that are to be returned to pasture or rangeland as herbicide options may be limited (Hargis and Redente, 1984). The information provided by pre-construction soil surveys, (i.e. topsoil and subsoil depths and descriptions) is of great importance when planning a successful reclamation. The use of pre-site assessments with advanced precision technology such as geographical information systems (GIS), can be adopted by updating soils maps with topsoil and subsoil depths. This way, machinery can accurately remove the correct amounts of soil, initially preventing soil mixing, ultimately improving productivity and reducing time to reclamation.

Conclusions

The contents within this review can be utilized by (1) landowners who are using these soils as a medium for plant production, (2) consultants who are expected to monitor and make recommendations to reclaim these soils, and (3) companies/industries who own or are responsible for the installation of the pipeline, mining of subsoil products, or the creation of well pads. By understanding the changes in soil nutrient availability and pH and reasons for said changes, landowners can comprehend and appreciate their soils more with educated consultants providing them with proper advice to manage disturbed soils.

Economic benefit will also be seen by all parties involved. By spending more money on the front end to first determine the correct amount of topsoil and secondly, taking the time and effort to separate and replace topsoil and subsoils, will likely save companies time and money. Finally, this information is also transferable to multiple disciplines with pipelines being installed for uses such as water, sewage, and fiber optic cables, in addition to oil and gas industries. The changes in soil properties during well pad development and surface mining practices are applicable to a suite of large construction projects such as street construction and site development, soil borrowing areas for highway construction, reshaping the landscape for subdivisions and landfills, and any other earthwork project that involves removal and replacement of soil materials.

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CHAPTER 2. PHOSPHORUS SORPTION AND DESORPTION OF SOILS TREATED BY THERMAL DESORPTION

Abstract

Thermal desorption (TD) is an effective way to remove hydrocarbons from soil. Soil exposure to temperatures between 200 and 500 °C, to volatilize hydrocarbons, can alter soil chemical properties that have potential to change phosphorus (P) dynamics. A series of laboratory soil sorption and desorption experiments were conducted on native and TD-treated soils to determine behavior of P in light of availability for plant uptake and risk for run-off. The average relative increase in P sorption after TD-treatment was 19.5% as shown by S_{max} values. This increase is likely due to the potential creation of biochar materials and mineral transformations of Fe- and Al-oxides during TD treatment causing increase in the soil's P sorption capacity. Dissolved organic carbon association with P did not influence sorption. Desorption of P was least in TD-treated soils indicating that the interaction between P and binding sites were strong. The amount of P retained by these soils (S_{max} values) may be of agronomic concern and should be considered when developing fertility plans. Based on these results, there is no apparent threat to nearby surface waters (k values) when using TD-treated soils for agricultural use.

Introduction

Oil and natural gas production in North Dakota has amplified in the past decade, and is associated with increases in environmental disturbances. With the North Dakota portion of the Bakken Formation being the third largest producing oil field in the United States (US EIA, 2018), the likeliness of accidental releases remains high (Mason, 2012). Along with natural areas, most crude oil spills in North Dakota occur on lands under agriculture production (cropland or rangeland), and contain petroleum hydrocarbons (PHC) that have the potential to decrease soil function and plant growth (Roy and McGill, 1998; Eom et al., 2007). Mechanisms for declined productivity may include toxicity (Timmerman et al., 2002), reduced seed germination (Yi et al., 2016), and depleted microbial communities (de Jong, 1980; Timmerman et al., 2002). There is a clear need for remediation of these soils for both human and environmental health, but remediation efforts that do not decrease soil function will allow for decreased time for reclamation to be successful.

A number of approaches have been used to remediate crude-contaminated soils and include, but are not limited to, bioremediation, incineration and relocation of soil material to landfills (i.e. dig and haul) (Diphare and Muzenda, 2014; Lim et al., 2016). The method known as TD has been proven effective in removing PHCs from soils allowing for soil material to be re-used for agriculture purposes (Hamby, 1996). The process of *ex situ* low temperature TD requires heating of the PHC contaminated soil to 350 °C for 15 min in a primary drum desorber, which allows contaminants to volatilize and achieve a desired concentration of <1500 mg kg^{-1} PHC. Treated soil from the primary drum desorber is then brought to a designated water content, cooled, and conveyed to stock piles for further cooling and eventually respreading. The volatilized PHCs and dust from the primary drum desorber are passed into a baghouse where the particulates are collected and the gases are separated and piped into an oxidizer. In the oxidizer, the PHC contaminants are ignited and leave the system entering the atmosphere as carbon dioxide and water vapor (Fig 6) (USEPA, 1994).

Thermal desorption has been proven effective in environments with petroleum, diesel fuel, and metal contamination (Hamby, 1996; Bonnard et al., 2009; Ouvrard et al., 2011). Compared to other methods of remediation, such as incineration, TD uses a lower heating temperature in a low-oxygen environment which reduces the amount of carbon emissions and is more time efficient than land farming (Onwurah et al., 2007). Thermal desorption also treats large volumes of soil that are available for re-use, which eliminates the need for a landfill (Hamby, 1996). Normally, successful remediation is gauged by the level of PHC in the soil after TD with little to no consideration for its ability to support plant growth or function in terms of nutrient cycling and plant nutrient availability (O'Brien et al., 2016). Reduction of PHCs to certain concentrations is not always a sufficient indicator of success in terms of returning the soil to agriculture productivity. In regards to agriculture productivity and soil function, assessment of soil nutrient availability and behavior are better indicators of remediation success.

Fundamental and baseline research has been done on the physical, chemical, and biological impacts of TD on soils (Falciglia et al., 2011; Tatàno et al., 2013; McAlexander et al., 2015; O'Brien et al., 2016; Ritter et al., 2017; O'Brien et al., 2017b; O'Brien et al., 2017c O'Brien et al., 2018). However, nutrient dynamics are an important consideration that have yet to be evaluated. Previous work on TD soils suggests that there is a significant decrease of soil organic carbon (SOC) after TD treatment due to direct combustion and the loss of soil aggregation (O'Brien et al., 2016), minimal influence on cation selectivity (Ritter et al., 2017) and nitrogen (N) cycling enzymes and ammonia oxidizing microbial communities remain functional after land application (Ritter et al., 2017). However, the behavior and availability of other key essential nutrients, such as phosphorus (P), remains unknown.

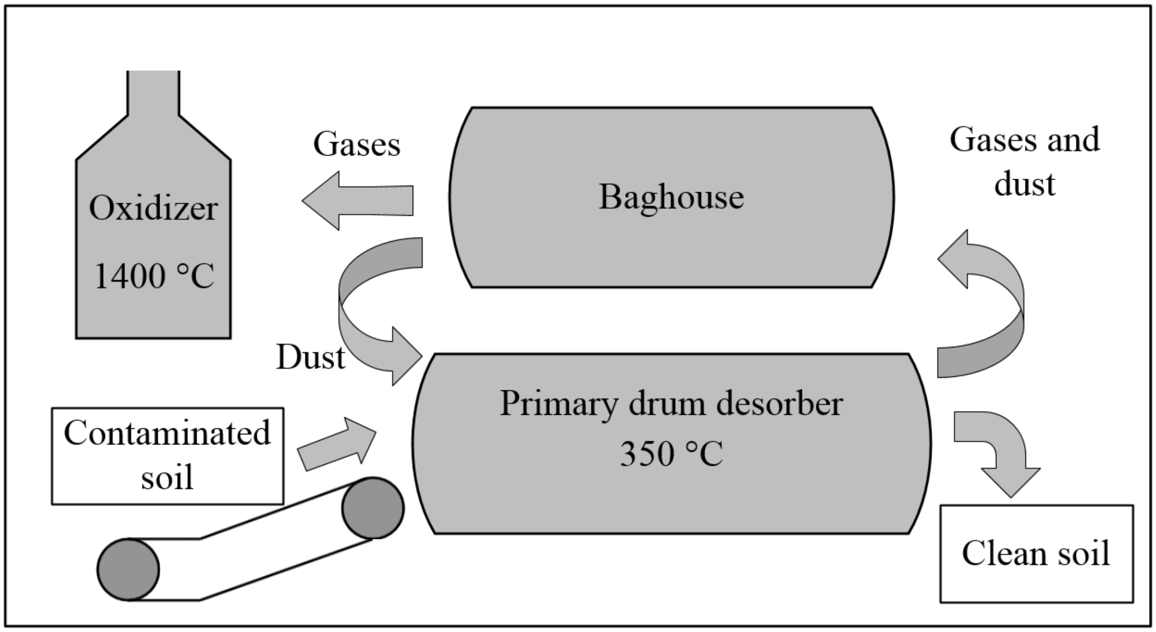

Figure 6. Diagram of the thermal desorption process (O'Brien, et al., 2016).

Phosphorus is the second most essential nutrient for plants (after N), often a limiting nutrient, and a factor in environmental non-point source pollution (Mays et al., 2000; Kruse et. al. 2015). From an agronomic perspective, optimal P ranges for plant productivity in the western regions of ND and across a majority of the northern Great Plains are approximately 8-16 mg kg^{-1} P for hard red spring wheat, corn and forage/hay grasses (Franzen, 2018).

While P is an essential nutrient for plants, it poses risks to water quality. Environmentally, multiple levels of dissolved P have been considered acceptable in waters across the US. Critical levels of dissolved P in lake systems, specifically, are suggested to be 0.01 mg L^{-1} (Sawyer, 1947; Vollenweider, 1968). The US EPA has established guidelines of up to 1 mg L^{-1} in streams, and certain areas of agricultural production are allowed 10 mg L^{-1} of dissolved P in their run-off waters while concentrations as low as 0.01 mg L^{-1} can create environmental problems such as eutrophication (USEPA, 1986; Sharpley et al., 1996). On the same note, particulate P can be lost to wind erosion and deposited into nearby water sources which is of concern in this region of the state.

Clay content and type, organic matter, and pH are a few important soil properties that influence P sorption and desorption in soils (Solis and Torrent 1989; Lilienfein et al., 2004; Zehetner and Miller, 2006; Pal, 2011). Maximum P sorption capacities have been estimated from <50 to >50,000 mg L^{-1} in soils with varying mineralogy and chemical properties (Auxtero et al., 2008). However, typical maximum P holding capacities in smectite dominated soils, such as those found across the northern Great Plains and used in this study, fall within the range of 240-820 mg L^{-1} with k values between 0.07-2.0 L mg^{-1} (Sui and Thompson, 2000; Hongthanat et al, 2011). Furthermore, dissolved organic carbon (DOC) can increase the amount of sorption sites in soils by ligand exchange and metal bridging (Fox and Comerford, 1990; Tan, 1998; Guppy et al., 2005) and when P associates with organic complexes, it becomes unavailable for plants (Donald et al., 1993; Guppy et al., 2005; Kruse et al., 2015). The increases in DOC seen in previous research (O'Brien et al., 2016) may influence P behavior in TD soils and be detrimental to nearby waters as P may move readily with DOC molecules via water as runoff or into groundwater.

Understanding P dynamics in TD soils is crucial for developing post-treatment fertility recommendations, thus ensuring that farmers are properly fertilizing their soils for optimum plant growth while reducing the amount of P loss to runoff into adjacent waters. Therefore, the objective of this study was to evaluate P availability in soils before and after TD treatment using sorption and desorption isotherms and the impact that DOC may have on P dynamics. By creating graphed relationships between the amounts of P bound to the soil surface and the amount left in solution after equilibrium (Mead, 1981; Tellinghuisen et al., 2010), sorption isotherms and their parameters allow for assumptions on P availability for plants and risk for P loss to runoff to be made.

Materials and Methods

Soil Sampling

Site Description

Due to a pipeline leak in 2013, surface and subsurface soils were impacted by a 21,000-barrel release of Bakken crude oil in northwest North Dakota (48°31'34.5"N, 102°51'25.72"W) totaling a surface area of 6 ha reaching 15 m deep. The soils at the site were mapped as Williams-Zahl complex loams

(Williams: fine-loamy, mixed, superactive, frigid Typic Argiustoll; Zahl: Fine-loamy, mixed, superactive, frigid, Typic Calciustoll) (USDA-NRCS, 2015) and at the time of the spill were cropped to Durum wheat (*Triticum durum*). Samples of non-oil contaminated topsoil (A horizon; TS) and subsoil (SS), and crude-contaminated stockpiled soil (SP) which had a total petroleum hydrocarbon concentration of <2,000 mg kg^{-1} were used in this study. Subsamples of each were also treated using an RS 40 Thermal Desorption/Oxidation unit at 350 °C for 10 min to create TD-treated topsoil (TS-TD), subsoil (SS-TD) and crude-contaminated stockpile (SP-TD). All samples were air-dried and ground to pass through a 2-mm sieve and analyzed for general soil properties (Table 3). pH and EC were determined with electrodes on a 1:1 soil:water slurry, CEC was determined by Mg-NH_4OAc exchange, and Olsen P and Mehlich P values were acquired per the Olsen (1954) and Mehlich (1984) methods. Total C and inorganic C were determined by using a Primacs TOC Analyzer (Skalar Analytical B.V., Breda, The Netherlands). Soil organic carbon (SOC) was then calculated as the difference between total organic carbon (TOC) and inorganic carbon (IC). This experiment was set up in a 3x2 factorial arrangement evaluating the differences before and after TD treatment.

Table 3. Soil chemical characteristics of soils used in this study including pH; IC, inorganic carbon; OC, organic carbon; EC, electrical conductivity, CEC, cation exchange capacity, Olsen P and Mehlich P.

Soils†	pH	IC	OC	EC	CEC	Olsen P	Mehlich P
		------mg kg^{-1}------		dS m^{-1}	cmol$_{(+)}$ kg^{-1}	---------mg kg^{-1}---------	
TS	7.7	0.25	2.82	0.39	22.4	14	39
TS-TD	7.9	0.31	1.98	0.92	17.6	65	141
SS	8.0	0.56	1.52	0.25	20.7	5	17.5
SS-TD	8.2	0.58	1.09	0.89	18.9	47	105
SP	8.2	1.48	0.34	0.96	16.4	6	7
SP-TD	8.1	1.43	0.26	1.07	16.6	7	8.5

†TS, native, non-contaminated topsoil; SS, native non-contaminated subsoil; SP, crude-contaminated subsoil; TD-treated topsoil (TS-TD), subsoil (SS-TD) and crude-contaminated stockpile (SP-TD)

Phosphorus Sorption

To measure P sorption, a SERA-IEG 17-recommended batch experiment procedure was used (Graetz and Nair, 2009). Two grams of each soil were weighed into 100-mL polyethylene centrifuge tubes and 50 mL of the corresponding concentrations of P: 0, 5, 10, 25, 50, 75, and 100 mg P L^{-1} as potassium phosphate (KH_2PO_4) prepared using 0.01 M $CaCl_2$. Each soil with each concentration was replicated 4 times. The soil suspension was shaken at room temperature (25 °C) for 24 hr on a horizontal shaker (180 osc min^{-1}) followed by centrifugation at a relative centrifugal force of 650 × *g* for 10 min. The supernatant was then filtered through 2 μm filter paper (CAT No. 1002110), of which 25 mL was removed using a pipette and solution P was determined using EPA method 365.1 (US EPA, 1993) with flow injection (FIAlab 2500). The remaining solution was removed from the tubes using a pipette and stored in glass scintillation vials for further analysis.

Phosphorus that was not detected in solution was assumed to be sorbed by the soil (Graetz and Nair, 2009). Both Freundlich and Langmuir Isotherm models were fit to the sorption data. The Freundlich equation is expressed as:

$$\mathrm{S} = K_F C^{1/n} \tag{1}$$

Where S (mg kg^{-1}) is the soil-bound P concentration after equilibration, C (mg L^{-1}) is the aqueous P concentration after equilibration, K_F (L mg^{-1}) is a constant value that relates to the bonding energy or affinity P has for soil, and 1/n (unitless) is an empirical fitting parameter related to the shape or linearity of the isotherm.

The Langmuir equation is expressed as:

$$\frac{C}{S} = \frac{1}{kS_{max}} + \frac{C}{S_{max}} \tag{2}$$

Where S and C are defined as in the Freundlich equations (Eq. [2]). S_{max} (mg kg^{-1}) is the maximum concentration of P that a soil has the capacity to bind, and k (L mg^{-1}) is the sorption coefficient related to the bonding energy or affinity P has for soil.

Freundlich (K_F and $1/n$) and Langmuir (k and S_{max}) parameters were estimated by inversely fitting Eqs. [1] and [2] to the measured S (dependent) and C (independent) experimental data. A nonlinear least squares method (Tellinghuisen et al., 2010) in the statistical software JMP 11.2.0 (SAS Institute, Inc.) was used to iteratively optimize (second-derivative, Newton-Raphson) the Freundlich and Langmuir isotherm parameters to achieve the best fits of Eqs. [1] and [2] to the measured data. The upper and lower confidence limits of the optimized isotherm parameter estimates were determined using $\alpha = 0.05$.

To determine the effects that DOC may have on P dynamics, 10 mL of the original supernatant was added to 20-mL glass autoclaveable tubes and 5 mL of alkaline persulfate digestion reagent (Patton and Kryskalla, 2003). Samples were then digested in an autoclave with a temperature of 132 °C and pressure of 117.2 kPa for 60 min, allowed to cool, and then analyzed for P using EPA method 365.1 (US EPA, 1993) with flow injection (FIAlab 2500). The difference between the total amount of P in the digested solution and the undigested solution was the amount of P associated with DOC (Fig 7). Dissolved organic carbon was assumed as non-purgeable organic carbon, carbon that remains after the sample is acidified and exposed to gas.

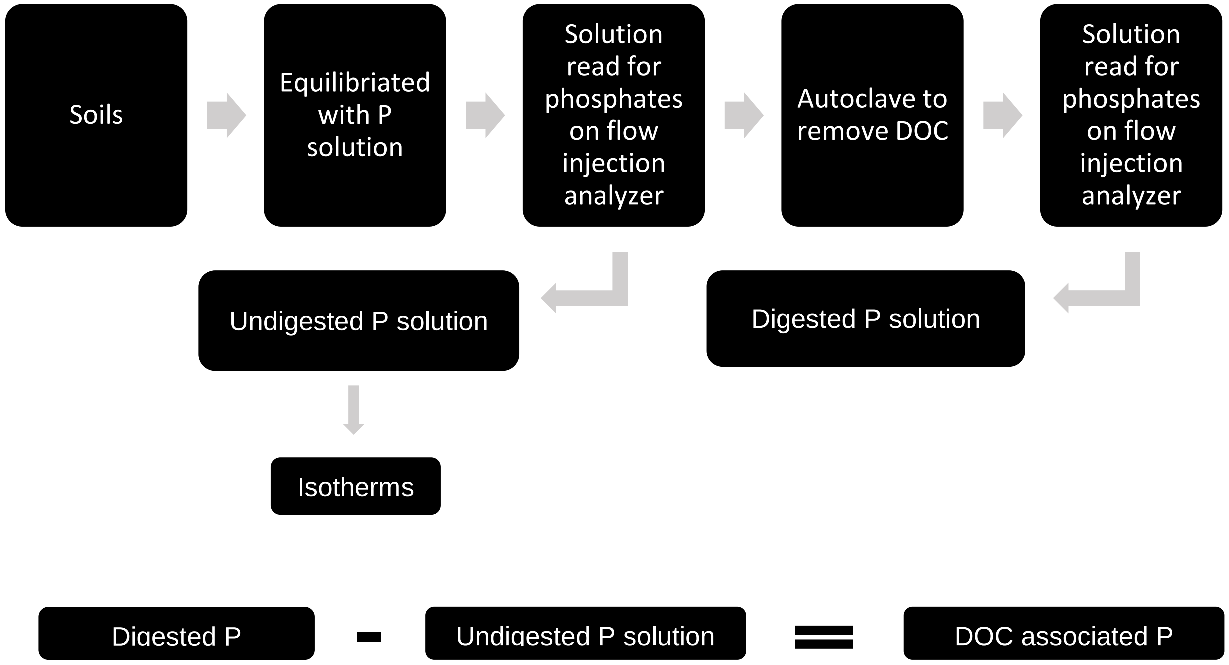

Figure 7. Flow chart of experimental design regarding isotherm development and DOC associated P.

Phosphorus Desorption

Phosphorus desorption characteristics were determined using adapted methods from Elrashidid and O’Connor (1982), Auxtero et al. (2008), Lair et al. (2009) and Yang et al (2014). Supernatant from the sorption experiment was removed using a pipette and discarded. To each tube, 30 mL of 0.01 M $CaCl_2$ was added, shaken, and centrifuged as noted above, followed by the removal of 10 mL for quantification of P using EPA method 365.1 (US EPA, 1993) with flow injection (FIAlab 2500) and 18 mL stored in glass scintillation vials. This process was repeated three times with 28 mL of 0.01 M $CaCl_2$ being added each time. The fourth and final desorption wash included addition of 28 mL of 0.05 M $NaHCO_3$ followed by shaking, centrifugation, and P quantified in the supernatant.

Statistical Analysis

Means of DOC-associated P for each soil treatment were compared using a one-way analysis of variance (ANOVA) with post-hoc Tukey HSD tests for specific treatment-level differences. Statistical significance was determined at the $\alpha = 0.05$ level. Desorption results were handled similar to sorption data with statistical tests performed using JMP 11.2.0 (SAS Institute, Inc.).

Results and Discussion

Soil Characteristics

Phosphorus sorption and desorption are dependent upon many basic soil characteristics, including clay content, pH, organic matter, soil cations (e.g. Ca and Mg) and Fe and Al oxides (Holford, 1997; Nascimento et al., 2018). Phosphorus sorption is known to decrease with increasing pH (Lopez-Hernandez and Burnham 1974; Bomans et al., 2005); however, soil pH was minimally altered after TD treatment. All soils in this study had a common pH value of about 7.6. Additionally, the EC values for all soils were very similar with an overall average of 0.7 dS m^{-1} (Table 3). The study soils are likely to retain nutrients like P, owing to their loam to clay loam textures dominated by smectite and illite clay fractions (O'Brien et al., 2016) with high surface area and retention via anion and ligand exchange (Edzwald et al., 1976).

Phosphorus Sorption

The parameter estimates resulting from the Freundlich and Langmuir isotherm fits to the measured data are presented in Table 4 and 5, respectively. For each case, the Langmuir (Table 5) model fit the P sorption data best compared to the Freundlich model, with the exception of the TS-TD soil, according to the R^2 values (Table 4). For each soil, identical 1/n values were optimized for the Freundlich model in order to properly compare the impact of TD on K_f. In each case, the TD treatment resulted in greater K_f estimates, indicating the TD treatment increased P sorption capacity.

Parameter estimates from the Langmuir model have greater physical meaning, and indicated that the maximum amount of P the soil can hold at one time (S_{max}) and the bonding energy (k) or the affinity P has for soil surfaces both increased as a result of the TD treatment (Table 5). In addition, the 95% confidence levels (CL) do not overlap (Fig 8), which indicates an increase in P sorption after TD treatment in SP and SS soils. Across all soils, S_{max} and k values were compared to previous published values of top and subsoils with similar soil characteristics to the study soils in this experiment. S_{max} and k values were reported as 375 mg L^{-1} and 0.05 mg L^{-1}, respectively in Chintala et al. (2014) and ranged between 357-667 mg L^{-1} and 0.14-0.52 mg L^{-1} in Hongthanat (2011). The S_{max}, of our soils ranged from 311-466 mg kg^{-1} (Table 5) while the k values were relatively low varying from 0.08 to 0.22 L mg^{-1}.

Soils with the lower k values, such as the SP soils, have a greater risk of P entering into solution, becoming highly mobile, and potentially lost. However, plant uptake requires phosphate ions in solution, so some soluble P may be considered an advantage from an agronomic perspective. The S_{max} values reported in our data indicate that an average of 71.67 mg L^{-1} of P was taken out of availability for plants after TD treatment. . Amounts such as this could be detrimental for crop productivity depending on the nature of the soil's fertility and respective fertility plans. For example, TS and SS soils started out with adequate amounts of P to sustain plant production (Olsen and Mehlich P) and when those soils were treated with TD, more P became available indicating either a replenishment of available P from the labile pool from previously bound organic matter P (Table 3) (Holford, 1997). However, SP soil that started with little organic matter, available, or labile P and did not experience that flush after TD, so it will require proper fertilizer additions if treated SP soils are used as a medium for plant growth. In addition, fertility should be monitored in years following TD treatment, as the initial flush of P is likely to occur only once, and once depleted plant yields may suffer as well. Holford and Mattingly (1976) documented ryegrass grown on soils containing approximately 100 mg^{-1} kg $soil^{-1}$ were taking up between 27 and 49 mg kg^{-1} of P. Thus, the removal of 71.7 mg L^{-1} of P from solution onto soil binding sites in TD-treated soils may be detrimental to plant productivity. Depending on the initial soil P level and with proper nutrient monitoring and fertility plans this can be avoided.

Although North Dakota has not established a P threshold for waters, Sharpley et al. (2003) states that if Mehlich P is greater than 150 mg kg^{-1}, further applications of P are to be avoided with buffers along water sources. None of the soils in our study contained Mehlich P values greater than 150 mg kg^{-1}, indicating that there should be no concern for water impairment. The bonding energy (k) can be used to assess the risk of P loss from soil materials to water sources with SP soils being of highest risk. However, there are no published criteria using k values alone to predict loss of P from soil (Hongthanat et al., 2011).

Table 4. Freundlich isotherm parameters estimates and 95% confidence limits (CL) and associated coefficient of determination (R^2) for each soil treatment (n=4). Standard error included in parentheses.

Soils	K_f	K_f Lower CL	K_f Upper CL	1/n	R^2
	----------------------L kg^{-1}----------------------				
TS	125.4 (12.3)	100.6	151.2	0.23	0.85
TS-TD	186.3 (15.8)	154.1	218.8	0.23	0.70
SS	91.5 (8.4)	74.8	109.2	0.27	0.83
SS-TD	172.1 (8.9)	153.9	190.5	0.27	0.69
SP	61.7 (7.8)	46.5	78.7	0.33	0.89
SP-TD	100.5 (10.3)	80.1	122.4	0.33	0.88

Table 5. Langmuir isotherm parameters estimates and 95% confidence limits (CL) and associated coefficient of determination (R^2) for each soil treatment (n=4). Standard error included in parentheses.

Soils	S_{max}	S_{max} Lower CL	S_{max} Upper CL	k	R^2
	------------------mg L^{-1}------------------			---L mg^{-1}---	
TS	404.2 (24.5)	357.5	460.0	0.17	0.85
TS-TD	456.9 (27.6)	403.5	518.8	0.21	0.66
SS	386.6 (15.9)	355.9	421.8	0.12	0.94
SS-TD	466.2 (21.5)	424.0	512.9	0.26	0.81
SP	311.0 (17.9)	277.2	352.6	0.08	0.91
SP-TD	392.1 (14.9)	362.9	424.5	0.14	0.94

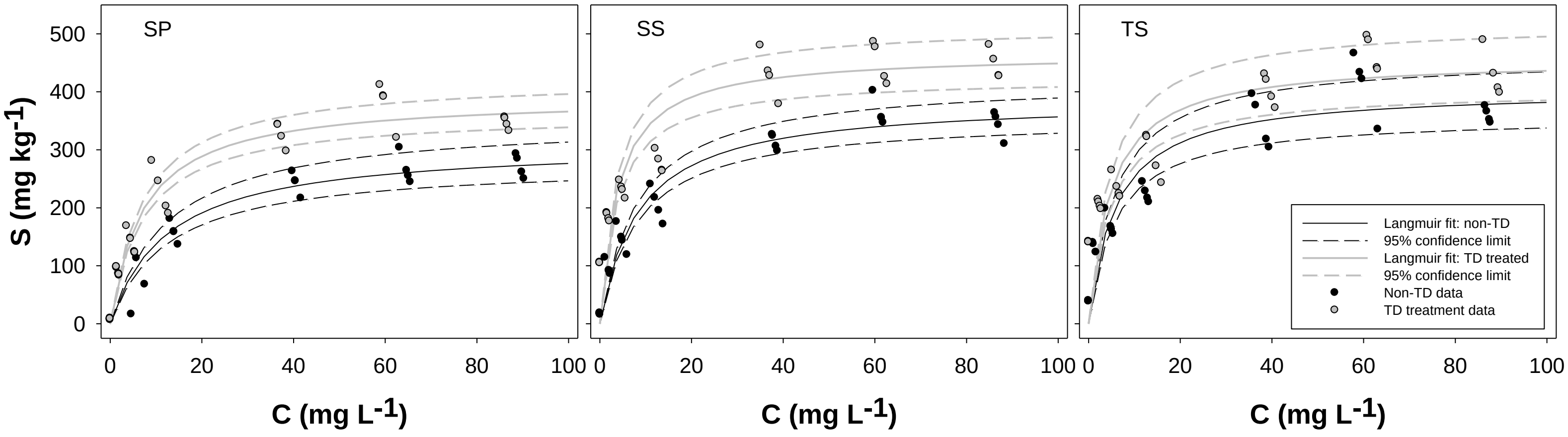

Figure 8. Langmuir isotherms for each soil treatment (n=4), grouped by TD treatment with 95% CL. Phosphorus solid phase concentrations (S) are the dependent variable and aqueous phase concentrations (C) are the independent variable.

DOC-associated P

Previous research by O'Brien et al. (2016) shows that DOC increases significantly in soils treated with TD (Fig 9), which creates concern for nutrient uptake and potentially nutrient loss in TD-treated soils. In the TS and SS soils, the DOC levels increased by at least three times after they were thermally desorbed, but DOC in the SP soils did not change. This increase in DOC is largely due to the initial amount of OC present in the soils; SP material comes from depths up to 15 m below the soil surface and contains little to no organic material to begin with. Conversely, TS and SS materials are closer to the surface where organic C inputs and storage capacities are higher. In addition, these soils have had more exposure to weathering and farming practices resulting in larger fluxes of soil C.

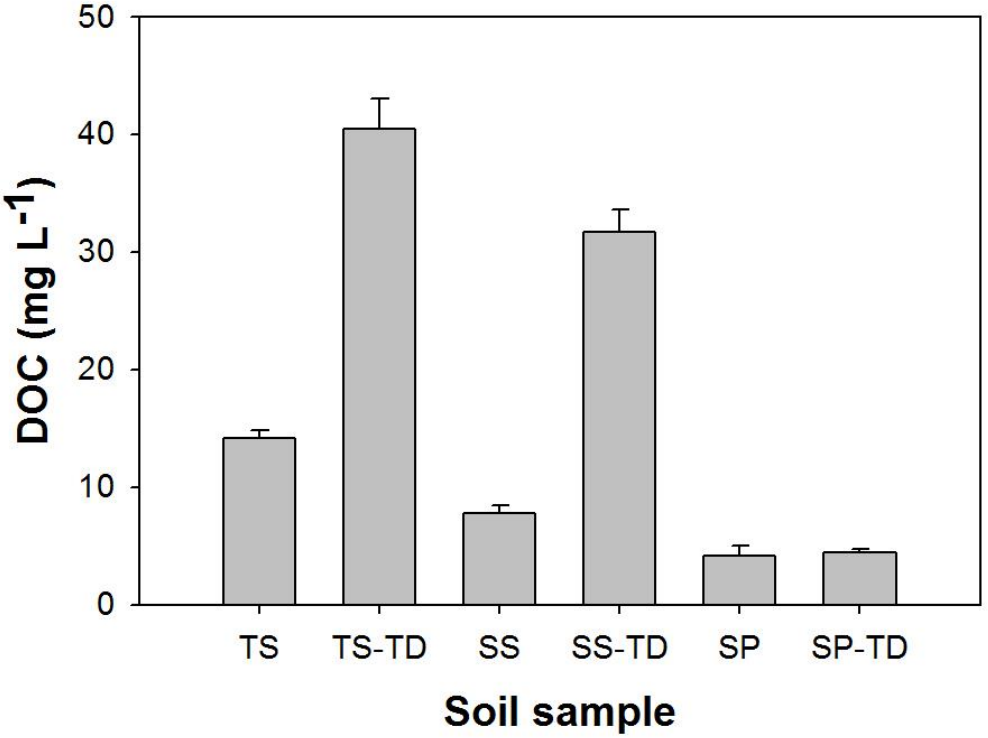

Figure 9. DOC values in TS, TS-TD, SS, SS-TD, SP, and SP-TD with error bars representing one standard deviation (n=3). Previously published data from O'Brien et al (2016).

Organic compounds have been reported to tie up and act as a transport mechanism for P (Donald et al., 1993; Guppy et al., 2005). The highly mobile DOC-P complex is a foreseen potential mode of nutrient loss in soils with very high organic presence. Forest-dominated environments produce soil horizons with high volumes of humic and fulvic organic acids that may tie up P or act as a mode of transportation for the P to waters (Jagadamma et al., 2012; Bol et al., 2016). Although TD treatment increased DOC levels, the amount of P associated with DOC after TD treatment was not significant at the 95% confidence level (data not shown). P sorbed after TD treatment to the TS was not significant, but sorption to SS and SP were significant. Dissolved OC was most elevated in TS-TD soils which indicates that DOC was not the reason for increases in P sorption because the greatest increase in sorption was found in SS-TD and SP-TD soils where DOC increases after TD were of less magnitude. Since the DOC-associated P was not increased by TD ($\alpha = 0.05$) for any of the soils, the likelihood of off-site transport with DOC should be minimal.

The methods used for this research only accounted for the removal of dissolved forms of OC rather than dissolved and colloidal. There is speculation that the elevated levels of DOC could be a combination of dissolved and colloidal organic compounds. Future research questions could address characterizing the specific organic compounds released by TD and their associations with P molecules.

Explanation of increased sorption after TD may be attributed to the conversion of organic compounds during thermal treatment to biochar (Vidonish et al., 2016; O'Brien et al., 2018). If pyrolysis occurred, organic surface area would increase allowing for more opportunities for P sorption (DeLuca et al., 2009; Mukerjee et al., 2011; Xu et al., 2014). Although biochar surfaces are characterized by their negative surface charges, anions such as phosphate are still able to sorb to such sites by ligand-bonded divalent cations such as Ca and Mg or other metals including Fe and Al (DeLuca et al., 2009). Biochar was not quantified nor characterized in these soil samples but the speculation has also been made in Ritter et al. (2017). In situations where biochar was used as an amendment into soil systems, the Fe and Al content was the dominant factor in P sorption (Xu et al., 2014). Thus, another mechanism potentially responsible for increased sorption is the alteration of Fe and Al oxides during TD treatment which provide highly preferred sorption sites by P ions (Piersynski et al., 2005; Lair et al., 2009). Substantial amounts of Fe and Al in biochar materials has been documented (Xu et al., 2014), solidifying the theory of Fe and Al and biochar causing increased P sorption.

Phosphorus Desorption

Phosphorus desorption, or the removal of P from soil binding sites, is an equally important parameter in determining potential P uptake by plants. However, desorption relationships are not studied as extensively as sorption (Raven and Hossner, 1994). Desorption curves are included in Figure 10, illustrating the relative amount of P desorbed from the solid phase with each rinse, and at varying initial P concentrations. Phosphorus was bound more tightly to the TS followed by SS and SP across all concentrations, which is directly related to the k value from the sorption isotherms. Here again, the ability for TS to retain more P is likely due to more OM while SS and SP soils are deeper in the profile with less OM. Desorption of P from TS-TD, SS-TD, and SP-TD soil consistently indicated that the TD treatment was changing something in the soil causing it to retain more P (dashed lines in Fig 10), which could be the strong bond between P and Fe- and Al-oxides.

As depicted in Figure 10, there is an obvious pattern with respect to the initial P concentration. As the initial P concentration increases from 0 to 100 mg P L^{-1} the amount of P desorbed or P released into aqueous solution increased and can be attributed to the concentration gradient between the solid and aqueous phase. Concentrations such as 0 mg L^{-1} are at very low levels compared to 100 mg L^{-1} at very high levels causing more P to be pulled into the aqueous phase in attempt to achieve equilibrium (Pierzynski et al., 2005).

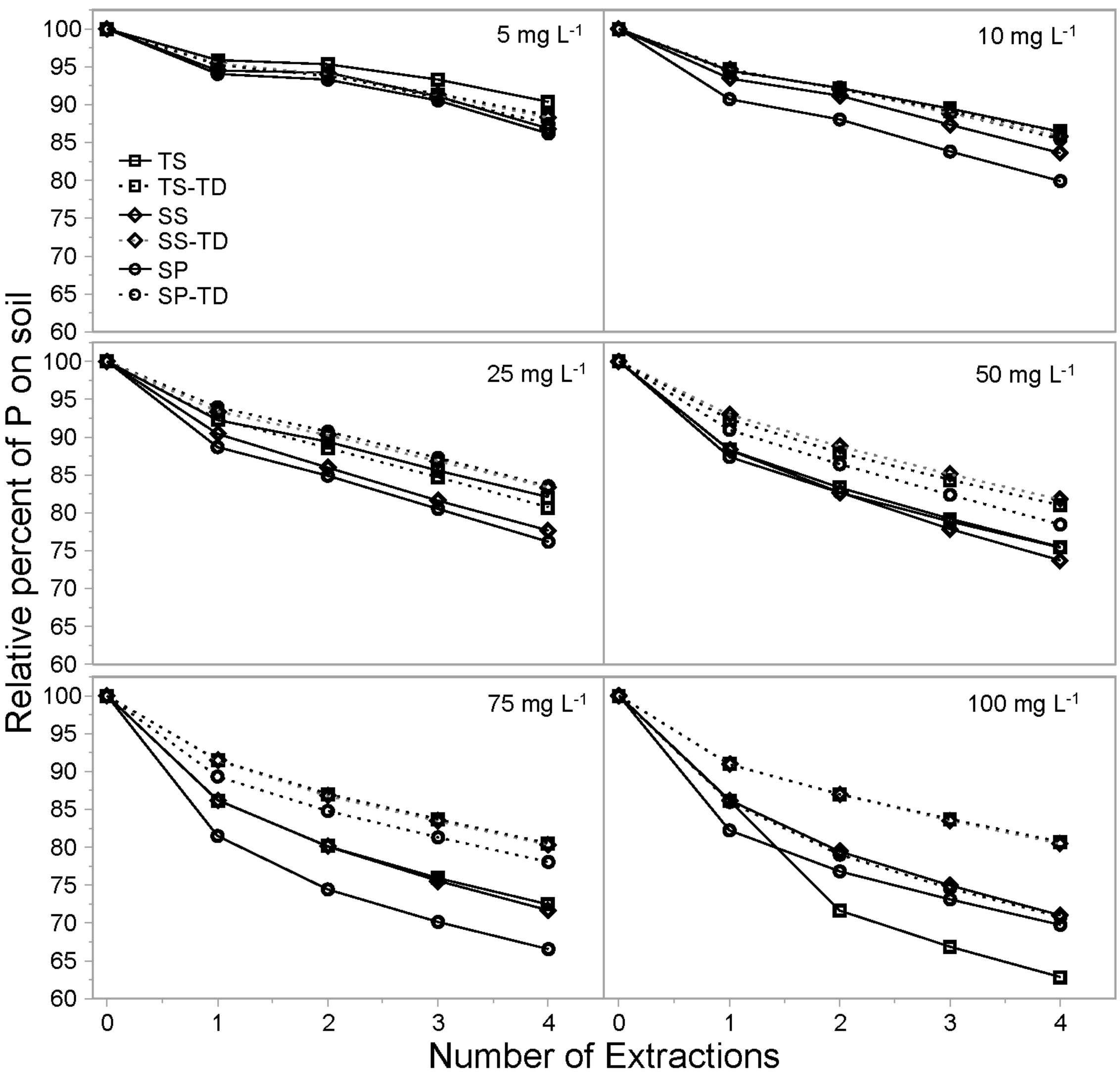

Figure 10. Relative desorption curves for TS, TS-TD, SS, SS-TD, SP, SP-TD at each initial P concentration (n=4).

Conclusions

The goal of this study was to determine the sorption and desorption characteristics of P on soils before and after TD-treatment. The overall success of reclamation is directly related to plant productivity which is dependent on the fertility of remediated soils. Soils from an active remediation site treated with TD show no immediate threat to nearby surface and ground waters. There should be extra precautions taken when developing fertility plans as P becomes less available for plant uptake in soils that are treated with TD, according to k and S_{max} values. Finally, there is no association of P with organic complexes of dissolved size fractions that are created during the high temperatures of TD treatment, therefore no risk for P movement by DOC transport.

In cases where these soils are used in agriculture production, successful remediation should require monitoring of essential plant nutrients. Phosphorus needs to be available for crop production, but not overly available leading to contamination of adjacent waters. Sorption and desorption isotherms may be used as a proxy to predict the behavior of P, helping maintain environmental quality and make responsible fertility management decisions that lead to successful TD treatment reclamations. However, commercial lab P tests should be sufficient in determining fertilizer recommendations on TD-treated soils, such as any other agricultural soil.

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CHAPTER 3. FIELD STUDY – CROP PRODUCTIVITY IN HIGHLY DISTURBED AND THERMALLY DESORBED SOILS

Abstract

The largest economical drivers in North Dakota are agriculture and oil and gas industries. However, there can be detrimental effects on agriculture when accidental releases of oil and gas products occur. A remediation method for removing crude oil from the soil, thermal desorption (TD), heats the soil between 200 and 500 °C under low oxygen conditions allowing hydrocarbons to volatilize, leaving soil with lower, acceptable levels of hydrocarbons. However, the process of TD impacts soil physical, chemical, and biological properties, which can hinder soil function and crop productivities. A field study was conducted to quantify crop production and soil properties of soils subject to TD. Field plots were established using native non-contaminated topsoil (A), crude contaminated subsoil (SP), thermally desorbed soil (TDU), 1:1 blends of A with SP or TDU, and with and without composted manure. Hard red spring wheat was grown in 2016 and 2018 and field peas in 2017. Relative yields were significantly greater in plots containing A compared to only TD or SP soils alone, and actual yields ranged from 1.33, 0.68, and 1.40 in SP soils to 2.77, 4.54, and 2.89 Mg ha^{-1} in the A horizon soils for 2016, 2017, and 2018, respectively. Soil organic carbon was also significantly greater in the A or A-mixtures but after three years there was no significant differences in 0-15 cm aggregate stabilities across all soil treatments. TD-treated soils or subsoils may be acceptable options for use as topsoil but mixing A horizon is highly recommended for facilitating successful soil reclamation.

Introduction

Oil and natural gas production in the Bakken region of North Dakota has increased significantly in the last decade, primarily due to the integration of horizontal drilling and hydraulic fracturing technologies (U.S. EIA, 2018a). During the peak of the most recent boom, the state was producing approximately 1.2 million barrels of oil per day (North Dakota Department of Mineral Resources, 2018), landing it’s spot as the second largest crude-oil producing U.S. state since 2012 (U.S. EIA, 2018b). With this increase in activity has come accidental spills and releases of oil and oil-produced waters that have degraded soil function in both natural (Robson et al., 2004) and agricultural systems (Issoufi et al., 2006) leading to decreases in plant production and net economic returns. The presence of released products, which are sometimes very mobile, may also negatively impact human health (Ruby et al., 2016), further supporting the need for proper reclamation methods.

A number of approaches have been used to remediate crude-contaminated soils. (Diphare and Muzenda, 2014; Lim et al., 2016). The most suitable remediation techniques are decided after first assessing the spill and determining the best approach as each situation is unique. One method, thermal desorption (TD), has been proven effective in removing petroleum hydrocarbons (PHC) from soil allowing for it to be re-used for agriculture purposes (Hamby, 1996). The process requires heating of contaminated soil to 350 °C for 10 to 15 minutes in a primary drum desorber which allows for contaminants to volatilize and achieve a desired concentration of <1500 mg kg^{-1} PHC. Clean soil is then brought to a designated moisture content, cooled, and is ready for re-use (USEPA, 1994). This method has been successful in remediating petroleum, diesel fuel, and metal contaminated environments (Hamby, 1996; Bonnard et al., 2009; Ouvrard et al., 2011).

Available research on TD has focused on the physical, chemical, and biological impacts on soils (Falciglia et al., 2011; Tatàno et al., 2013; McAlexander et al., 2015; O’Brien et al., 2016; O’Brien et al., 2017a; O’Brien et al., 2017b; Ritter et al., 2017; O’Brien et al., 2018). For example, TD treatment may increase soil pH (Sierra et al., 2016; Yi et al., 2016), transform and decrease SOM (Kiersch et al., 2012; O’Brien et al., 2016), and can be detrimental to microbial biomass presence and activity (Pape et al., 2015). To date, less attention has focused on plant productivity and influencing soil parameters (O’Brien et al., 2017a) but for a holistic assessment of TD treatment, crop productivity on these highly disturbed soils needs to be considered.

The length of time that reclamation projects require is directly connected to increased costs for the responsible party and decreased agricultural products to the land owners. So, minimizing the time needed for reclamation is important for all persons involved. Given that an end-goal of reclamation is to bring disturbed soils to their pre-disturbance functions, there is a need to evaluate the productivity potentials of these soils when used for agricultural purposes. Therefore, the objective of this field study was to determine the productivity potentials of TD-treated and oil-containing subsoils and whether they can be acceptable replacements for topsoil compared to native, non-oil containing topsoil.

When thinking about the length of time it takes for a soil system to recover after a major disturbance, Figure 11 illustrates the effectiveness of additional reclamation efforts. In the event of a disturbance, which could be physical alteration like removal and replacement, or the introduction of a foreign material such as crude-oil or brine, soil function is reduced and without any interference its trajectory line may hold a slope of zero with the time prediction to any sign of improvement being decades. However, when these soils are remedied of their contaminant by processes like TD, this effort may reduce the time to original condition. In this Figure 11 the, the reference soil is the uncontaminated A horizon with the goal of reclamation to reach 90-110% soil productivity relative to the this A. Moving even further up on the “soil condition or treatment” and by adding amendments or cropping systems to the soil may allow for an even shorter time to reclamation.

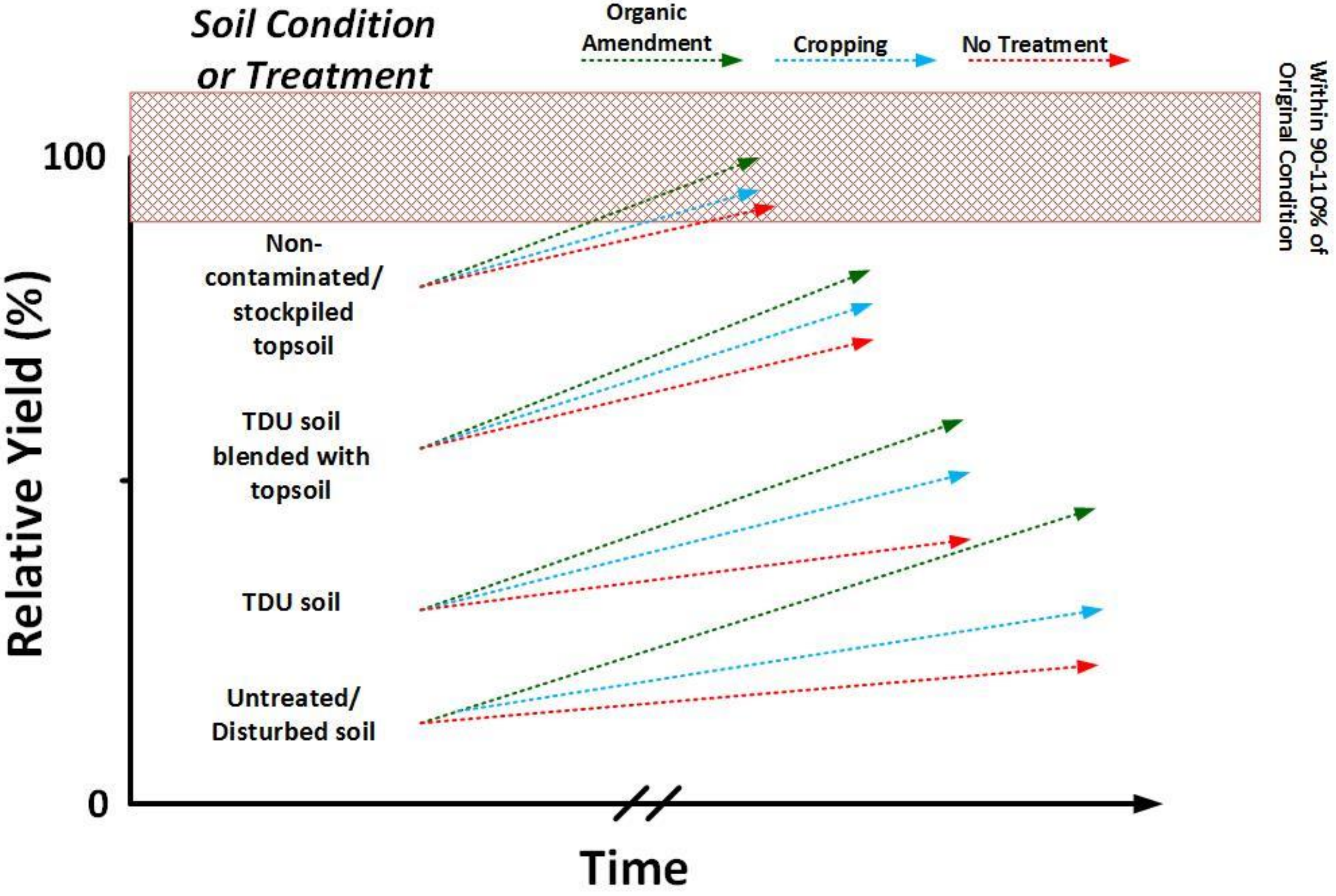

Figure 11. A conceptual diagram of time to recovery of soil function/productivity to 90-110% of original condition in soils that are disturbed. Arrows represent potential linear trajectories with and without additional reclamation efforts. See figure 3 for more detailed trajectory as time to reclamation is not always a linear trend.

Materials and Methods

Site Description

In 2013 a pipeline leak resulted in a 21,000-barrel crude-oil release in Mountrail County, North Dakota (48°31’34.5”N, 102°51’25.72”W) (Fig 12) which impacted 6 ha of surface and subsurface soils. Bakken crude-oil is a light (API gravity 42), and sweet (sulfur < 0.2%) variety with low viscosity and properties similar to water which allowed it to travel nearly 15 m below the soil surface making this spill, to date, the largest terrestrial crude-oil spill in the United States (O’Brien et al., 2018).

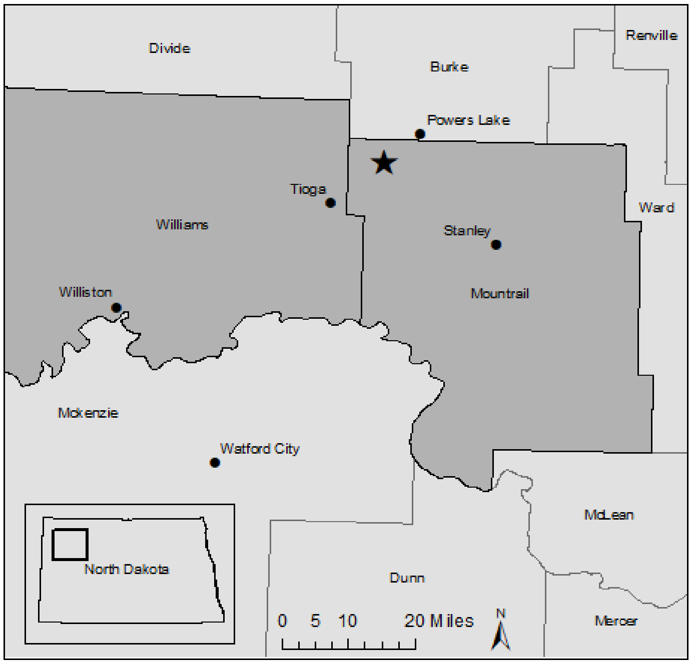

Figure 12. Diagram with star depicting research location in Mountrail County, ND.

Adjacent to the site of remediation, 17 m x 15 m x 0.9 m field plots consisting of mixtures of three different soil materials were constructed. A total of 10 soil treatments included: 1) a control of non-oil contaminated topsoil (A) that was mapped as Williams-Zahl complex loams (Williams: fine-loamy, mixed, superactive, frigid Typic Argiustoll; Zahl: Fine-loamy, mixed, superactive, frigid, Typic Calciustoll) (USDA-NRCS, 2015); 2) crude-contaminated stockpiled subsoil (SP), which had a total petroleum hydrocarbon concentration of <2,000 mg kg^{-1}, collected from up to 15 m below the soil surface; 3) SP soil that was treated with an RS 40 Thermal Desorption/Oxidation unit at 350 °C for 10 min to create thermally desorbed material (TDU); 4) 1:1 mixtures of SP and A (SP + A); 5) 1:1 mixtures of TDU and A (TDU + A);

6) A + m (where m represents 45 Mg ha^{-1} of cattle feedlot composted bedding mixed into the top 15 cm of soil); 7) SP + m; 8) TDU + m; 9) SP + A + m; and 10) TDU + A + m. Plots were organized in a randomized complete block design (RCBD) and replicated three times (Fig 13) (O'Brien et al., 2017b). Soil characteristics are provided in Table 6. Further details about plot construction and their uniformity can be found in O'Brien (2017b).

The Köppen-Geiger climate classification of the study region is Bsk (arid, steppe, cold arid) (Kottek et al., 2006). Total growing season precipitation in 2016, 2017, and 2018 was 433, 231, and 464 mm while total potential evaporation total 1206, 1298, and 1026 mm, respectively (NDAWN, 2016-2018). Although the 2016 and 2018 seasons had near normal precipitation, in 2017 the region experienced a major drought and the research location received 148 mm below the 30-yr average (National Climatic Data Center, 2011).

Table 6. Previous data (O’Brien et al., 2017b) including mean values (with standard deviations) for physical and chemical variables of soil treatments used in this study. Treatments are A) native, non-contaminated topsoil; TD) contaminated subsoil material treated by thermal desorption; SP) crude oil contaminated subsoil material; TDU + A) 1:1 mixture, by volume, of A and TD; and SP + A) 1:1 mixture, by volume, of A and SP.

Treatment	A	TDU + A	TD	SP + A	SP
Variable† (unit)	Mean (sd)				
PAW (cm^3 cm^{-3})	11 (1.2)	11 (1.1)	10 (1.0)	11 (1.2)	11 (1.2)
SSA (m^2 g^{-1})	84 (8.1)	86 (6.7)	92 (9.4)	98 (8.4)	104 (8.7)
Sand (g kg^{-1})	455 (29)	451 (15)	434 (19)	423 (19)	389 (12)
Silt (g kg^{-1})	327 (21)	321 (18)	326 (25)	325 (19)	345 (19)
Clay (g kg^{-1})	219 (27)	228 (17)	239 (22)	252 (16)	345 (19)
IC (g kg^{-1})	3 (2)	11 (3)	16 (1)	11 (3)	16 (1)
SOC (g kg^{-1})	21 (4)	11 (2)	3 (1)	11 (3)	5 (1)
pH	7.4 (0.2)	7.8 (0.1)	8.1 (0.1)	7.8 (0.2)	8.1 (0.1)
EC (dS m^{-1})	0.3 (0.1)	0.6 (0.1)	0.8 (0.2)	0.7 (0.1)	1.0 (0.2)
N (mg kg^{-1})	28 (5.7)	19 (2.3)	8.5 (1.3)	11 (3.9)	5.2 (1.8)
P† (mg kg^{-1})	9 (1.9)	7.0 (1.3)	3.3 (1.5)	4.9 (1.6)	2.1 (0.7)
K (mg kg^{-1})	248 (20)	227 (16)	193 (9)	192 (24)	148 (12)
Ca (mg kg^{-1})	3220 (505)	4360 (201)	4710 (14)	4300 (283)	4550 (146)
Mg (mg kg^{-1})	636 (69)	670 (106)	691 (40)	861 (182)	998 (80)
Na (mg kg^{-1})	17 (1.9)	56 (9.4)	114 (17)	55 (13)	95 (18)
Zn (mg kg^{-1})	0.8 (0.2)	0.8 (0.1)	0.8 (0.1)	0.5 (0.1)	0.4 (0.2)
Fe (mg kg^{-1})	49 (15)	25 (3.8)	10 (1.1)	24 (7.0)	11 (2.1)
Mn (mg kg^{-1})	51 (44)	29 (12.7)	25 (4.9)	17 (6.5)	12 (4.8)
Cu (mg kg^{-1})	1.2 (0.2)	1.2 (0.1)	1.3 (0.1)	1.2 (0.1)	1.3 (0.3)
Cl (mg kg^{-1})	1.9 (0.6)	10 (2)	20 (2.5)	5.2 (1.3)	8.9 (1.7)

†PAW, plant available water; SSA, specific surface area; IC, inorganic carbon; SOC, soil organic carbon; EC, electrical conductivity; P, Olsen P.

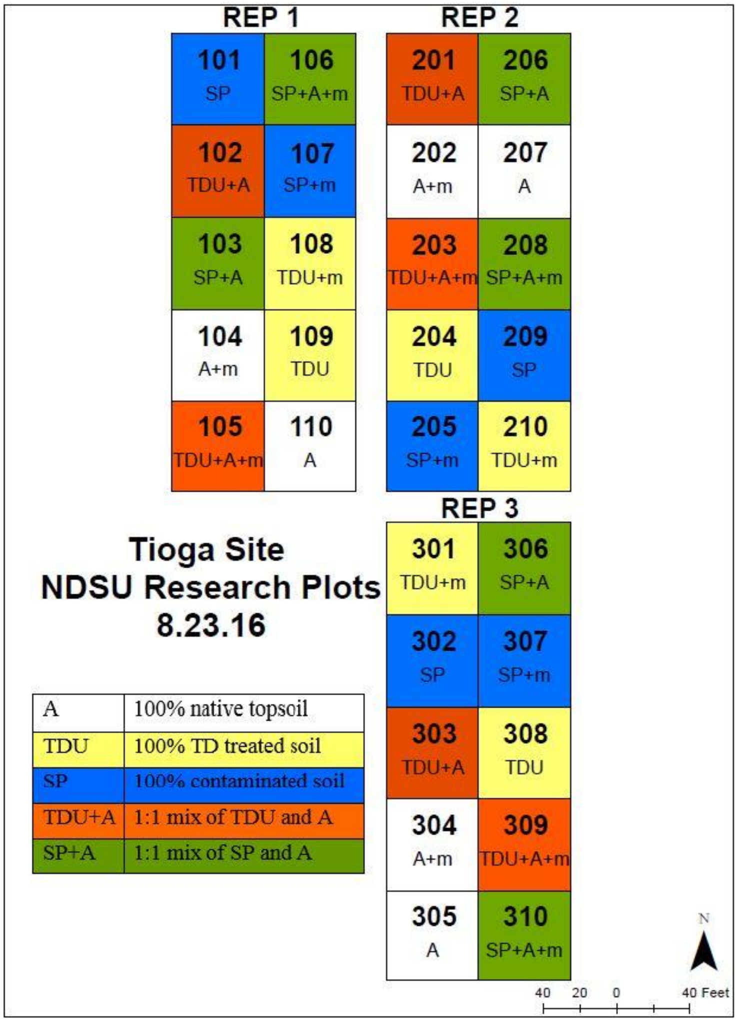

Figure 13. Field plots (17 m x 15 m x 0.9 m) organized in RCBD with soil treatment identification.

Wheat Yields, Field Pea Biomass and Qualities

The crop rotations and farm practices used in this study were determined based on common practices used by the landowner. Each spring prior to planting, fertilizer in the form of granular urea (46-0-0) and mono-ammonium phosphate (MAP) (11-52-0) were broadcasted to ensure that all plots met the proper fertility requirements to sustain the respective crop. Fertilizer rates were based on soil analysis and North Dakota recommendations (Franzen, 2018). In 2016 and 2018 hard red spring wheat (HRSW) (*Triticum* aestivum) varieties Barlow and Glenn, were seeded day of year (DOY) 142 and 136, using an air seeder (2016) and small plot drill seeder (2018) at populations of 100 and 116 kg ha^{-1} in 30 and 15 cm rows, respectively. Weed control was accomplished by pre-emergence application (rates) of Roundup®

(2.34 L ha^{-1}) and in-season broadleaf herbicides application of 2,4-D ester (0.58 L ha^{-1}) and Everest (0.05 L ha^{-1}) in 2016 and of Bison® (2.92 L ha^{-1}) and Starane® (0.98 L ha^{-1}) in 2018. Disease pressure was controlled by fungicide application of Propistar® (0.07 L ha^{-1}) in 2018. Using a small plot research combine, 15 m^2 from each plot were harvested DOY 235 in 2016 and DOY 232 in 2018, and yield was corrected to 13.5% moisture.

In 2017, field peas (*Pisum sativum, L.*, variety Birdsall), were seeded DOY 129 by the landowner at a population 180 kg ha^{-1} 30 cm rows using an air seeder. Herbicide recipes (rates) for 2017 included Roundup® (2.34 L ha^{-1}), Sharpen® (0.15 L ha^{-1}), and Spartan® Charge (0.27 L ha^{-1}). Due to drought, peas were harvested (5 m^2 per plot) for forage on DOY 207 using a forage chopper. Biomass was dried at 60 °C for 72 hr and yield determined.

Grain samples of HRSW and forage samples of peas from each field year were ground to pass a 250 µm sieve and sent to Agvise Laboratories in Northwood, ND to be analyzed for total N. Total N values were then converted to crude protein using factors provided by Tkachuk (1966) and Holt and Sosulski (1979) for wheat and peas, respectively. Information on soil hydrocarbon degradation and hydrocarbon contents in the grain from these plots can be found in O'Brien et al. (2018).

Soil Sampling, Preparation and Analysis

Soil samples from the 0-15 and 15-30 cm depths from each plot were taken in the fall of 2015, and after harvest 2016, 2017, and 2018 using hand probes or bucket augers. All samples were air-dried and ground to pass through a 2 mm sieve. The two depths were used to calculate fertility parameters while the soil organic C (SOC) was determined from only the 0-15 cm. Fertility samples were sent to Agvise Laboratories in Northwood, ND and total C and inorganic C were determined by using a Primacs TOC Analyzer (Skalar Analytical B.V., Breda, The Netherlands). Soil organic carbon (SOC) was then calculated as the difference between total organic carbon (TOC) and inorganic carbon (IC).

Aggregate stability and size distribution were determined using the wet sieving protocol described by Six et al. (1998). For this metric, bulk samples were collected from the 0-15 cm depth from each plot not treated with composted bedding. From 50 g subsamples aggregates were separated into three fractions; free soil particles (0-53 µm), microaggregates (53-250 µm), and macroaggregates (250-2000 µm). Total aggregation was calculated by taking the sum of the micro- and macroaggregates.

Decomposition rates of plant residues in soil treatments can serve as a proxy for evaluating soil function, especially in anthropogenic influenced soils (Harmon et al., 1999). By monitoring the breakdown of varying residues within residue bags, soil biological presence and activity in TD-treated soils can be better understood. In 2017 residue bags were created and installed using an adapted protocol from Daudu et al. (2009). Residue or litterbags are Fiberglass mesh bags, measuring 15.3 cm by 30.5 cm, filled with 15 g of air-dried alfalfa (*Medicago sativa*) or 10 g of air-dried rye (*Lolium perenne L.*). Two types of residue were chosen based on their differing C:N ratios of 10.5:1 and 50:1 for alfalfa and rye, respectively. As microbial communities require a diet with a C:N ratio of 24:1, we can infer that incorporation of alfalfa residue will be broken down faster and result in excess N to be made available for plant use. Rye, on the other hand, will be slowly broken down because of a high ratio, and N will be scavenged from the soil system during the decomposition process (Harmon et al., 1999). Residue bags were placed on the surface of all plots that did not receive composted bedding in the spring of 2017 and remained for two growing seasons. After harvest of 2018 residue bags were collected, residue was washed of excess soil, oven-dried at 60 °C for 24 hours, and weighed to determine mass loss of residue.

Volumetric soil water content was measured in 2017 and 2018 from all plots that did not receive compost bedding using the PR2 Profile Probe by Delta-T Devices (Delta-T Devices, Cambridge, United Kingdom) at depth increments of 100, 200, 300, 600, and 1000 mm. Access tubes were installed each spring and removed after harvest. Water content was measured bi-monthly beginning after planting until after harvest. Given the rooting depths of the crops, the values for the top 300 mm were averaged each sampling day.

Statistical Analysis

Differences in mean yield, grain quality, and SOC between soil treatments were assessed using a 2-way analysis of variance (ANOVA) and Tukey-Kramer's range post hoc with an alpha level of 0.05 and 0.001 with year and soil treatments as factors (SAS version 9.4, proc glimmix). Treatment means for aggregate stability and residue bags were assessed with a Wilcoxin non-parametric model (proc npar1way) while soil water content was compared across treatments using an ANOVA with repeated measures to account for sampling times (proc glimmix). All statistical analysis was conducted in SAS version 9.4 software.

Results and Discussion

Relative Yield

The main focus of this study was to determine the suitability of TD-treated soil as a replacement for topsoil on agricultural lands. Thus, the A horizon treatment was considered as the reference condition, and relative yield was assessed as the ratio of yields from each treatment to this control. Relative yields allow for treatment comparisons across the three years and two different crops. Soil treatment was the only effect found significant; year and the interaction between year and soil treatment were non-significant (Table 7). Actual yields (with standard deviations) ranged from 1.33 (0.14), 0.68 (0.54), and 1.40 (0.35) in SP soils to 2.77 (0.82), 4.54 (2.85), and 2.89 (1.05) Mg ha^{-1} in the A horizon soils for 2016, 2017, and 2018, respectively. These values provide context to the range of yields between the control, or reference condition and no reclamation action after contamination (SP).

Irrespective of the starting soil condition, soil with A blended into the mixes produced significantly greater yields than the stand-alone soils such as SP and TDU. The addition of composted bedding, at the rates used in this study, were not effective at increasing crop yields on SP and TDU soils, which indicates that the rate of application was not high enough. Currently, the State of North Dakota does not have regulations or standards on soil function after oil or produced water spills other than guidelines regarding the negative impact on surface and ground waters. However, coal-mined lands are subject to federal and state regulations on soil productivity where successful reclamation is measured by meeting the criteria stated in performance standards, article, 69-05.2-22-07 (North Dakota Legislative Branch, 2018). Aside from the year requirements within the performance standards, if the 90% statistical confidence crop performance standard, compared to a reference area (e.g. control plot), was used as a guide, plots having A would have met this standard after the first year of cropping.

When compared to the county average and using the 90% performance standard, the yields on the plots were not fully recovered after the third year (NASS, 2016; NASS, 2017). However, native A horizon plots were within 0.16 Mg ha^{-1} of meeting that average.

Table 7. Mean values (with standard deviations) for relative yield (Mg ha^{-1}) relative crude protein content (%) in wheat grain and pea forage and soil organic carbon.

Effects	Variables	Relative Yield	Relative Crude Protein	Organic Carbon§
		Mg ha^{-1}	%	%
Year	2015	n/a	n/a	1.06 (0.66)
	2016	0.68 (0.27)	0.98 (0.14)	1.17 (0.72)
	2017	0.83 (0.67)	0.93 (0.10)	n/a
	2018	0.71 (0.24)	0.93 (0.12)	0.96 (0.57)
	Pr > F	ns	ns	**
Soil Treatment	A†	1.00‡	1.00	1.93 (0.92)b
	A + m	1.15 (0.56)a	0.98 (0.04)	2.26 (0.35)a
	SP + A + m	0.88 (0.27)a	0.98 (0.06)	1.17 (0.36)c
	TDU + A	0.82 (0.27)ba	1.02 (0.09)	1.10 (0.15)c
	TDU + A + m	1.09 (0.45)ba	1.02 (0.05)	1.09 (0.18)c
	SP + A	0.92 (0.55)ba	0.97 (0.06)	1.29 (0.26)c
	TDU	0.56 (0.15)bc	0.98 (0.11)	0.35 (0.1)d
	SP	0.39 (0.22)bc	0.75 (0.07)	0.53 (0.12)d
	TDU + m	0.40 (0.18)c	1.04 (0.07)	0.42 (0.1)d
	SP + m	0.47 (0.25)c	0.80 (0.08)	0.51 (0.16)d
	Pr > F	**	ns	**
Soil Treatment x Year		ns	ns	ns

* Significant at P < 0.05

** Significant at P < 0.001

† A: native A horizon; A + m: native A horizon with manure; TDU: thermally desorbed soil; TDU + m: thermally desorbed soil with manure; TDU + A: thermally desorbed soil with native A horizon; TDU + A + m: thermally desorbed soil with native A horizon and manure; SP: crude contaminated stockpiled soil; SP + m: crude contaminated stockpiled soil with manure; SP + A: crude contaminated stockpiled soil with A horizon; SP + A + m: crude contaminated stockpiled soil with A horizon and manure.

‡Values not available because compared to A horizon.

§OC values are not relative and include only 0-15 cm depth.

ns, Non-significant

Grain Quality

There were no significant differences in relative protein content across treatments and the year by treatment interaction was also non-significant (Table 7). For livestock feed, the preferred protein content for HRSW grain ranges between 13.5 and 18.6% (US Wheat, 2011), and the actual protein values in 2016 and 2018 ranged from 12.3 to 19.4% and 12.5 to 17.0%, respectively. In field pea forage, protein ranges from 18.0 to 20.0% (Endres et al., 2016), and our treatments ranged from 15.9 to 21.0%. Protein is one of the most important parameters when assessing HRSW and field pea quality because it can affect not only the palatability for livestock but also result in market cost variations when protein contents are found above or below the baseline percentage (US Wheat, 2011). When comparing protein from the treatments to these published target values, all treatments produced grain and pea forage that was acceptable for livestock feed. Thus, when crop productivity and livestock production are anticipated after TD treatment, grain quality should not be of concern as long as soil fertility recommendations are followed

Organic Carbon

Over the span of four years, there were significant differences in OC (Table 7). However, with the difference being only 0.22%, this was not considered a meaningful change. When comparing treatments, the differences were found between the soil mixes that include native A topsoil and the stand alone soils, SP and TDU, but the addition of m, at the rates applied for this study, were not great enough to increase OC above the unamended SP and TDU plots. After three years of cropping on these plots, an increase in OC was expected, especially in plots containing A horizon that are likely to have greater and more diverse biological communities sequestering more C (Fierer et al., 2002). Since there were no significant differences after three cropping years this timeframe may be too short given the crops grown and the climate of the region.

Aggregate Stability

Aggregate stability is an important factor in overall soil function and is often used as an indicator for soil quality because it integrates many soil physical, chemical, and biological properties (Tisdall and Oades, 1982). No significant differences were found when comparing the mean stability of soil aggregates across soil treatments (Table 8). Overall stability was approximately 85% across all soil treatments, meaning that 85% of soil particles are being considered either micro or macroaggregates. Aggregates from undisturbed grasslands and no-till managed soils have been shown to have higher overall stability and higher percentages (>90%) of macroaggregates compared to disturbed soils (Cambardella et al., 1993; Degens et al., 1996). However, in soils that have been disturbed, texture influences aggregation in the short term (1-5 years) (Wick et al., 2008), and the high aggregation values from the treatments may be attributed to the amounts of clay particles present, which typically increases aggregation (Degens et al., 1996; Wick et al., 2008) as seen with the 250-2000 µm macroaggregate size class dominating across all treatments. Along with improvements in infiltration (Six et al., 1998; Amézketa 1999), aggregate stability is closely correlated to soil biological process such as microbial activity and nutrient availability (Ladd et al., 1996; Denef et al., 2001; Essington 2004). There was an expectation that the A horizon and soil mixes that included A horizon would develop micro and macroaggregates faster because of increased microbial activity and organic matter. Again, three years may be too soon to see any differences across treatments in the development of soil structure and aggregation considering the extensive handling of these soils during TD treatment and plot construction (Wick et al., 2009; O'Brien et al., 2016). With that, these soils have suffered extreme disturbances from excavation during handling to the heating of TD-treatment, but the dominance of macroaggregates and high overall stability indicates that if TD-treated soils are used for agronomic purposes, stability should not be of a concern.

Table 8. Mean aggregate stability values and (standard deviations) for each size fraction and soil treatment. Percent mass loss and (standard deviations) of rye and alfalfa.

Effects	Variables	Aggregate Stability					Residue Bags	
		Overall Stability	Sieve Size µm					
			>2000	250-2000	53-250	<53	Rye	Alfalfa
				%			% Loss	
Soil Treatment	A	83 (5)	12 (1)	47 (4)	29 (4)	13 (1)	6 (27)	82 (7)
	TDU	85 (2)	26 (13)	33 (7)	28 (11)	13 (3)	5 (24)	88 (4)
	TDU + A	86 (4)	13 (11)	35 (8)	34 (5)	18 (4)	16 (15)	83 (4)
	SP	84 (3)	2.0 (4)	35 (9)	29 (6)	17 (2)	13 (8)	82 (11)
	SP + A	86 (2)	21 (14)	38 (2)	27 (12)	14 (3)	21 (11)	83 (9)
Pr > Chi-Square		ns	ns	ns	ns	ns	ns	ns

ns, Non-Significant

Residue Bags

With the temperature of TD treatment reaching 350 °C, soil biological diversity and activity are likely to subside (Cebron et al., 2011). The diversity and activity of soil biota play an important role in nutrient cycling for crop production (Pankhurst et al., 1995), and therefore, their recovery and activity is important after disturbance. Mean decomposition rates of two types of residue across soil treatments were not statistically different (Table 8). As expected, decomposition of alfalfa was greater than the rye residue, likely due to its low C:N ratio (10.5:1), compared to the rye's (50:1). The C:N of the alfalfa residue provides sufficient N to meet decomposer needs, and allows excess N to be made available for plant use. Conversely, the rye was not extensively decomposed in these soils, perhaps due to the high C:N ratios of this material requiring microbes to scavenge N and potentially creating N depleted soils. Incorporation of low C:N ratio material may introduce N into the system and improve overall soil health. In addition, water limitation, especially in the drought year of 2017 may have hindered decomposition. Although the results from the residue bags were statistically insignificant, one can infer that because the breakdown of alfalfa residues, microbial communities are present and active to some extent in all treatments. We can conclude that TD treatment or crude-oil contamination did not alter the ability of the soil to break down rye or alfalfa when compared to the A.

Soil Water Content

With the PET of the study region ranging from 2.2-5.5 times greater than growing season precipitation, water management and conservation are crucial to prosperous yields and reclamation success. The soil water content did not vary significantly across treatments within DOY (Fig 14), which may be the result of various soil properties within each soil treatment. For example, the A, which was expected to hold more water also hosted crops that were healthy and thus available water was used for plant uptake. In addition, the A exhibited an increased root presence (data not shown) which may have increased infiltration, allowing for water to move deeper into the profile below the root zone.

On the contrary, TDU soils consistently contained more soil water throughout the growing season, likely due to decreased plant growth, reduced water uptake, and more water remaining in the root zone. SP soils tended to hold adequate volumes of water as well which may be attributed to the increase in clay minerals of this soil that allows water to remain in the profile for longer periods of time (Nyeki et al., 2017). No significant differences across treatment indicate that the blending of A horizon with TD-treated soil is not likely to have any detrimental effects on plant available water as their water holding capacities were similar.

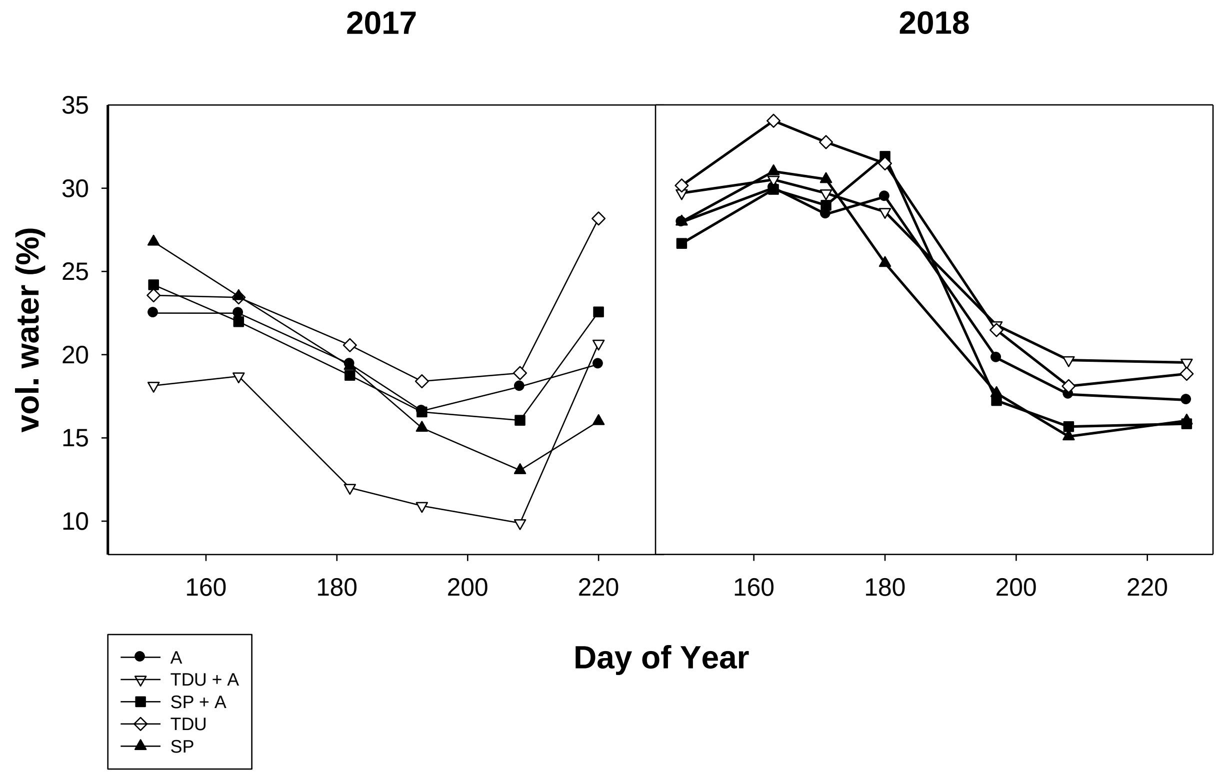

Figure 14. Mean percent volumetric water content (n=3) in the top 300 mm for 2017 (pea) and 2018 (wheat) growing seasons. Water content did not differ across treatments within day of year.

Other Agronomic Considerations

An interesting discovery was made during the 2017 field season when field peas were planted to the plots. Previously, in the fall of 2016 an herbicide that was labeled with little residual effect was applied to control broadleaf weeds. Western ND suffered extreme drought in 2017, causing the pea crop to produce less than average yields. The drought was thought to also spark some additional residual effects with the herbicide, causing abnormal characteristics in the pea roots. This hypothesis is justified by the fact that pea plant deformities (herbicide injury) were occurring to a greater extent in SP and TDU plots compared to A horizon plots. Furthermore, the SP and TDU plots may have contained less organic material or biological activity in the soil to bind and breakdown residual herbicide that otherwise would have degraded in a higher quality soil.

Studies investigating the persistence of herbicides in biochar substances may be applicable to this situation. During the TD treatment, SOC within the soil may have been transformed to biochar (Ritter et al., 2017). Assuming this did occur, herbicide is able to strongly sorb to the biochar which limits its availability to microbial communities that are present (Jones et al., 2011). As the microbial presence may be minimal in plots without A horizon included, herbicide breakdown is likely inhibited in SP and TDU plots compared to A treatments, as observed in the field. Although, Yu et al (2009) suggests that herbicides become less available for plant uptake when bound to biochar like materials, field peas are extremely susceptible to herbicide damage and expressed definitive herbicide injury symptoms leading us to believe this theory.

This was an important lesson in reclamation as weed control is one of the most important challenges in the industry, so it is likely that herbicides will be used for control on reclaimed soils. Thus, it is important to conduct a full soil analysis on a suite of properties and choose herbicides carefully. Extra precautions may need to be taken when herbicides are applied to TD-treated soils for agricultural purposes.

Conclusions

The main objective of this research was to determine the suitability of TD-treated soils as a substitute for topsoil in the event that current topsoil becomes contaminated. In short, the agronomic use of TD-treated soil may be an acceptable replacement for topsoil but mixing A horizon with TD-treated soils is an effective way to reach pre-spill yields soon after reclamation. When these soils were blended, SOC and water content were similar to concentrations found in the A horizon, which in turn will increase nutrient availability, aggregate stability, microbial activity and improvements of other soil properties. Consequently, in the situation where topsoil is unavailable to blend, yield reductions and longer recovery times are to be expected. Though there haven’t been yearly responses to our reclamation efforts, there has certainly been a treatment difference which indicates that the more effort and knowledge that is put into the reclamation process will impact the trajectory of reclamation. By incorporating A horizon with TD-treated or SP soils as a topsoil replacement, acceptable reclamation may be achieved more efficiently, especially in arid regions where water is limiting and a crucial component to success. To more completely answer questions regarding the use of TD-treated soils as a replacement for topsoil, the soil parameters accessed in this study, such as aggregate stability, residue bags, and OC should be investigated for a longer time periods. By doing so, increased knowledge on the temporal development of highly disturbed soils and their yield potentials can be obtained.

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GENERAL CONCLUSIONS

The general goal of this research was to determine the suitability of thermally desorbed soils as a replacement for topsoil in the event of a lack of topsoil after a large disturbance such as that of a crude-oil spill, in this instance. These highly disturbed oils can be used as a replacement for topsoil in agricultural production, but drags in crop yield and overall soil function are to be expected. However, by blending native non-contaminated topsoil with TD-treated soils as a medium for crop productivity can drastically improve soil properties. Phosphorus sorption and desorption characteristics in TD-treated soils were significantly different than non-TD soils. There is a possibility of TD treatment having an effect on the available P pool used for plant uptake, yet it was determined that there are no environmental concerns in regard to P. Furthermore, crop yields, soil water, and soil organic carbon were all found to be significantly higher in soils with a level of A horizon mixed in rather than TD-treated soil or crude-contaminated stockpiled soil alone. Overall, TD treatment significantly affected crop yields and soil chemical parameters, thus, if deciding to incorporate TD-treated soils into an agriculture production setting, necessary precautions should be taken.