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Pyrolytic Treatment and Fertility Enhancement of Soils Contaminated with Heavy Hydrocarbons

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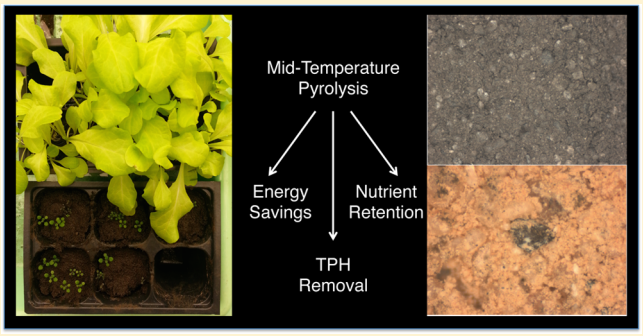
Supporting Information

ABSTRACT: Pyrolysis of contaminated soils at 420 °C converted recalcitrant heavy hydrocarbons into "char" (a carbonaceous material similar to petroleum coke) and enhanced soil fertility. Pyrolytic treatment reduced total petroleum hydrocarbons (TPH) to below regulatory standards (typically <1% by weight) within 3 h using only 40−60% of the energy required for incineration at 600−1200 °C. Formation of polycyclic aromatic hydrocarbons (PAHs) was not observed, with post-pyrolysis levels well below applicable standards. Plant growth studies showed a higher biomass production of *Arabidopsis thaliana* and *Lactuca sativa* (Simpson black-seeded lettuce) (80−900% heavier) in pyrolyzed soils than in contaminated or incinerated soils. Elemental analysis showed that pyrolyzed soils contained more carbon than incinerated soils (1.4−3.2% versus 0.3−0.4%). The stark color differences between pyrolyzed and incinerated soils suggest that the carbonaceous material produced via pyrolysis was dispersed in the form of a layer coating the soil particles. Overall, these results suggest that soil pyrolysis could be a viable thermal treatment to quickly remediate soils impacted by weathered oil while improving soil fertility, potentially enhancing revegetation.



INTRODUCTION

Crude oil spills pose significant risks for environmental damage, with over $10 billion spent in oil spill cleanup alone annually worldwide.[1−3] Although offshore oil rigs and tankers are responsible for occasional large-volume spills, 98% of oil spills occur on land, with an average of 70 spills per day (>25 000 per year) reported to the U.S. EPA.[4,5] Without adequate response, the effects of major spills could last decades.[6] Although bioremediation (e.g., landfarming and windrowing) can contribute to the cleanup of terrestrial oil spills, biodegradation of the heavy hydrocarbons that prevail after the oil is weathered is difficult to accomplish.[7−12] These heavy hydrocarbons represent an environmental hazard and a significant remediation challenge.

Thermal treatments of contaminated soils, such as ex situ thermal desorption (low temperature with varying O_2 levels)[13] and incineration (high-temperature combustion), may be better alternatives to landfill disposal because more of the contaminants are destroyed rather than being simply relocated.[14] Thermal technologies can be applied to a variety of contaminants, including PCBs, PAHs, and petroleum hydrocarbons.[15−22] Often done as a two-step sequential process or separately, thermal desorption and incineration can quickly remove over 99% of total petroleum hydrocarbons (TPH), including recalcitrant high-molecular-weight hydrocarbons.[14,15,23−26] The main drawbacks to these technologies are a high energy demand and decreased soil fertility due to the destruction of soil organic carbon and other nutrients.[23,27] Energy costs to provide sufficiently high temperatures for incineration (600−1200 °C) and thermal desorption (100−600 °C) can be high.[15,23,28] Pyrolysis could be achieved with lower temperatures (e.g., 350−500 °C for the conversion of hydrocarbons to char)[29−31] and accordingly, for similar reaction times, could decrease the required heat input (and associated energy costs) by approximately 40−60% relative to those of incineration.

Although some studies have shown that hydrocarbon removal by thermal desorption could aid in regreening efforts after land spreading of treated soil,[32] increased genotoxicity to earthworms was also observed following thermal desorption of PAHs at 500 °C at a coking plant, likely due to the increased bioavailability of residual contaminants or byproducts.[33] Therefore, technological innovation is needed for energy-efficient and safer thermal treatment of contaminated soils in a manner that also preserves soil quality. This study proposes such a strategy based on integrating pyrolysis and thermal

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Table 1. Analysis of Selected Soil Agronomic Parameters[a]

soil	C (%)[b]	TKN (mg/kg)	NO_3-N (mg/L)	P (mg/kg)	hydrophobicity	water-holding capacity (g water/g soil)	pH	CEC (meq/kg)
A, untreated TPH 15 000 mg/kg	3.09 ± 0.35	196.9	2.21	17.24	class 7: very hydrophobic	0.36	7.2	160.5
A, pyrolyzed (420 °C, 3 h) TPH < 4 mg/kg	1.35 ± 0.30	440.9	0.21	65.82	class 0: very hydrophilic	0.33	8.4	191.0
A, incinerated (650 °C, 3 h) TPH < 4 mg/kg	0.32 ± 0.11	38.8	0.14	3.81	class 0: very hydrophilic	0.34	11.1	300.4
B, Uncontaminated	0.53 ± 0.04	759.3	23.21	3.23	class 0: very hydrophilic	0.26	7.4	231.8
B, untreated TPH 19 000 mg/kg	5.51 ± 0.09	699.8	28.80	1.83	class 5: strongly hydrophobic	0.29	7.7	300.4
B, pyrolyzed (420 °C, 3 h) TPH 290 mg/kg	3.18 ± 0.41	411.4	0.24	0.36	class 5: strongly hydrophobic	0.27	9.0	240.3
B, incinerated (650 °C, 3 h) TPH < 4 mg/kg	0.46 ± 0.11	59.6	0.16	0.37	class 0: very hydrophilic	0.30	11.9	250.4

[a]Analysis provided by UGA Agricultural and Environmental Services Laboratories in Atlanta, Georgia. [b]Performed on a CHN elemental analyzer (Costech ECS 4010) at Rice University in Houston, Texas.

desorption techniques, producing a soil enriched in a material with some of the chemical properties of charcoal.

Pyrolysis byproducts (e.g., biochar) have drawn tremendous interest due to their potential to enhance soil fertility, sequester CO_2, and manage organic waste.[34−41] By pyrolyzing soils containing heavy hydrocarbons, we aim to create "char" out of the residual hydrocarbons and soil organic matter, thus generating a soil with some of the organic carbon that would be lost by incineration. In this paper, we test the hypothesis that pyrolysis can not only efficiently remove hydrocarbons while offering significant energy savings over incineration but may also enhance soil fertility relative to that of contaminated or incinerated soils. We evaluated the efficacy of pyrolytic treatment using microscopy and thermogravimetric and elemental analysis and by measuring agriculturally relevant soil parameters before and after treatment. This effort provided mechanistic insight on thermal transformations of heavy hydrocarbons and their effects on soil quality.

■ MATERIALS AND METHODS

Contaminated Soil Samples. We selected two soils for our study. Soil A was contaminated with heavy hydrocarbons with a total petroleum hydrocarbons (TPH) content of 16 000 mg/kg of soil. The TPH in this soil was a result of a crude oil spill at a wellhead and thus represents a complex mixture of hydrocarbons. As determined by X-ray diffraction, soil A was composed of 4% clays, 3% carbonates, 79% quartz, and 14% other minerals. Uncontaminated background soil A was not available from this site. Contaminated soil B had a TPH value of 19 000 mg/kg of soil. This soil was created by spiking topsoil from an arid region in Arizona with oily sludge from a crude oil production site. This uncontaminated ("background") soil B was composed of 12% clays, 10% carbonates, 31% quartz, 20% K-spar, 26% plagioclase, and 1% pyrite. An overview of the major soil characteristics of contaminated and pyrolyzed soils is included in Table 1.

Soil Pyrolysis and Incineration. Pyrolysis was performed in a stainless-steel 0.5 L fixed-bed reactor heated by a split-hinge tube furnace (Thermo Scientific Lindberg/Blue M) under continuous N_2 flow (1 L/min). Thermocouples recorded the temperatures on the outer surface of the reactor as well as in the center of the soil chamber of the reactor to monitor the temperature distribution and ensure the desired pyrolysis temperatures were reached through the reactor.[42,43] Volatiles and moisture exited through the reactor outlet into a trap flask, and gases were vented into a fume hood (Figure S1).

To compare soil pyrolysis to incineration, we also incinerated soils A and B in air at 650 °C for 3 h using a muffle furnace (Thermo Scientific Lindberg/Blue M). Soil incineration is typically conducted at higher temperatures in the field (600−1200 °C).[23] Our relatively low incineration temperature was chosen to compare pyrolysis with the least-destructive incineration strategy. Pyrolysis and incineration experiments were run in triplicate for each soil.

Weight Loss Analysis by Thermogravimetry. A thermogravimetric analyzer (TGA) (Q500, TA Instruments) was used to study soil weight losses occurring due to the thermal desorption of hydrocarbons or pyrolysis reactions. Samples of contaminated or treated soils were heated under N_2 using either a constant heating rate program or a step-isothermal technique developed to measure weight losses in different temperature ranges. Each sample was first heated to 100 °C and held there until its weight stabilized. That weight was considered to be the "dry weight" of the sample because moisture and, perhaps, some light hydrocarbons are released in this temperature range. The temperature was then raised to 150 °C and held there until again the sample weight did not change, thus ensuring that all desorption (or reaction) processes occurring in the 100−150 °C range had enough time for completion. This process was repeated by raising the temperature in 50−70 °C increments until reaching the final temperature. The differences between the sample weights measured at the end-point of each isothermal step provided the total weight losses for the temperature ranges of 100−150 °C, 150−200 °C, and so on.

GC Analysis of Solvent-Extractable Hydrocarbons and TPH Measurements. For both pyrolyzed and incinerated soils, we measured the solvent-extractable hydrocarbons via GC-FID (Agilent 7890A) based on EPA method 8015M.[44,45] Briefly, 5 g soil samples were vortexed and centrifuged with 20 mL of solvent. Due to differences in the composition of crude oils, different solvents were chosen for extraction (dichloromethane for soil A and carbon disulfide for soil B (Sigma-Aldrich)). Specifically, soil B contained more nonpolar waxy paraffins than soil A, making nonpolar carbon disulfide a more effective solvent choice. Samples were filtered through 1 μL syringe filters (Fisher Scientific) before gas chromatography−flame ionization detector (GC−FID) analysis. For an overall

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assessment of hydrocarbon removal, we examined changes in the area under the curve of the GC−FID chromatograms. A total of two such tests were run for every pyrolysis and incineration experiment (which were also done in triplicate).

TPH and PAH analysis was performed by Lancaster Laboratories (Lancaster, PA).

Soil Fertility and Plant Studies. We grew *Arabidopsis thaliana* and *Lactuca sativa* (Simpson black-seeded lettuce) in controlled growth rooms kept at 21 °C with 16 h of simulated sunlight provided by full-spectrum lamps at 140 μE m^{-2} s^{-1} (where E = einstein, defined as 1 mol of photons).[46,47] A total of five replicates were used for every soil and plant type. *Arabidopsis* was chosen as a standard in plant biology literature, and lettuce has been identified as the ideal plant for hydrocarbon-contaminated soil testing due to toxin sensitivity.[48] Soils were mixed, moistened, and packed into 50 mL pots with filter paper at the bottom to prevent soil loss. Half of the treatments were amended with quarter-strength Hoagland's solution[49,50] to assess the benefits of nutrient addition to pyrolyzed soil fertility. After the seeds were planted, the pots were stored at 4 °C for 2 days to synchronize germination and then placed in the growth room. Germination and seedling death was monitored for 21 days. After being harvested, the plants were then dried for 48 h at 65 °C and weighed. Standard error was calculated on plant germination and weights when possible. *Arabidopsis* seedlings were so small and delicate in incinerated, untreated, and hydrocarbon-contaminated soils that we were unable to weigh individual plants and thus unable to accurately calculate error.

Additional Soil Characterization. Properties of contaminated, pyrolyzed, and incinerated soils were analyzed using several methods common to biochar characterization. We performed elemental analysis in triplicate using a CHN analyzer (Cosctech ECS 4010), and determined water-holding capacity gravimetrically using the method described by Kinney et al.[51,52] Hydrophobicity was determined using a molarity of ethanol droplet (MED) test.[51,53] A total of six replicates were used for hydrophobicity and water-holding capacity experiments. Standard agronomic analyses were also made, as shown in Table 1 (measurements made at UGA Agricultural and Environmental Services Laboratory, Atlanta, GA). We acquired images at Rice University (Houston, TX) on an optical microscope equipped with a digital camera at 10−20× magnification.

RESULTS AND DISCUSSION

Soil Pyrolysis at 420 °C and Effective Removal of TPH to below Regulatory Limits. Pyrolysis of crude oil and its SARA fractions (saturates, aromatics, resins, and asphaltenes) is characterized by a low-temperature stage (100−300 °C) involving the volatilization (or distillation) of saturates and aromatics and a high-temperature stage (350−500 °C), during which resins and asphaltenes are pyrolyzed to produce petroleum coke.[29,54−60] The production of coke via the thermal cracking of asphaltenes and resins involves a complex reaction network that includes (a) the cracking of alkyl chains from aromatic groups, (b) the dehydrogenation of naphthenes to form aromatics, (c) the condensation of aromatics to higher fused-ring aromatics, and (d) dimerization and oligomerization reactions.[55,61−63] Asphaltenes are the main precursors of petroleum coke.[55,63] Their conversion to coke starts between 300 and 350 °C, proceeds rapidly in the 400−450 °C range, and is usually complete before the temperature reaches 500 °C.[30,64] Aromatics, paraffins, olefins, and naphthenes can also

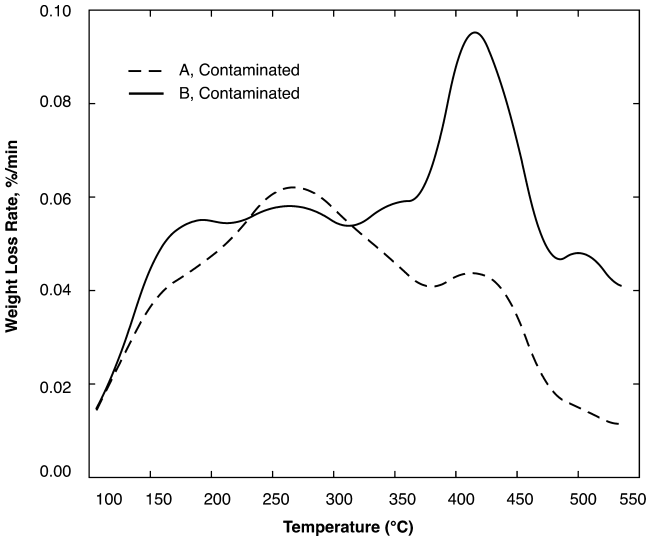

Figure 1. Thermogravimetic analysis showing weight loss rates of two hydrocarbon-contaminated soils. Samples were heated at a constant rate of 5 °C/min under flowing nitrogen. The curves reflect the devolatilization of light hydrocarbons for temperatures below 350 °C and removal by pyrolysis between 350 and 500 °C. For both soils, the pyrolysis reaction rates peaked in the 400−450 °C range.

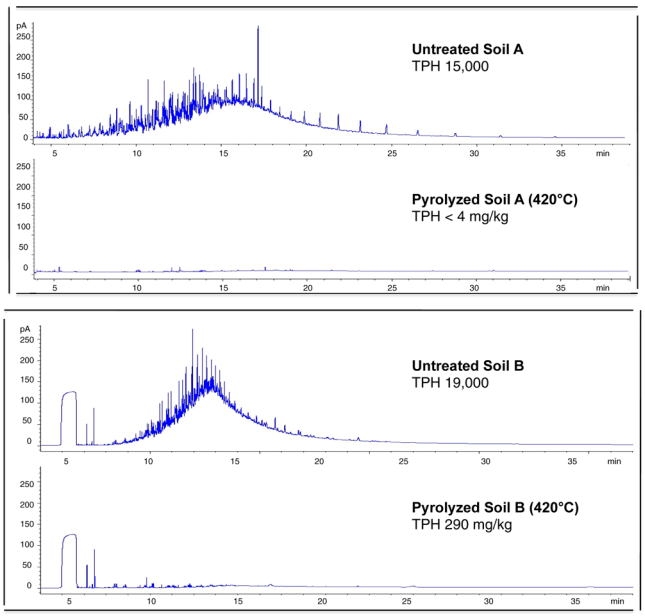

Figure 2. GC−FID analysis of soils A and B before and after pyrolysis treatment. Both soils show extensive removal of hydrocarbons and significant reduction in TPH.

contribute to coke formation via secondary reactions. However, these reactions have both long induction periods and low rates at the temperatures considered here.[55,65] More importantly, the inert gases flowing through our pyrolysis reactor continuously sweep the released volatiles and light hydrocarbons produced by cracking reactions, thus preventing the formation of coke via these secondary reactions.[55,65]

Although there are numerous publications on the homogeneous pyrolysis of hydrocarbons, very little is known about the effects of soil on the pyrolysis of oil dispersed in a porous medium.[66,67] Therefore, we carried out a series of thermogravimetric experiments to determine whether the well-established

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Table 2. Thermogravimetric Analysis of Two Soils Contaminated with Heavy Hydrocarbons before and after Pyrolytic Treatment or Incineration[a]

sample tested	% total weight loss (dry basis)	fractional loss in the 100−350 °C range	fractional loss in the 350−420 °C range
soil A, contaminated	2.46 ± 0.63	0.80	0.20
soil A, pyrolyzed[b]	0.40 ± 0.14	0.51	0.49
soil A, incinerated[c]	0.23 ± 0.23	0.75	0.25
soil B, uncontaminated	0.52 ± 0.23	0.66	0.34
soil B, contaminated	5.54 ± 1.03	0.71	0.29
soil B, pyrolyzed[b]	1.16 ± 0.44	0.44	0.56
soil B, incinerated[c]	0.44 ± 0.16	0.70	0.30

[a]The percent total weight loss represents averages from three runs (± one standard deviation). Uncontaminated soil samples (not available for soil A) were run to discern the weight loss associated with hydrocarbon removal through volatilization or thermal degradation. [b]Pyrolytic treatment was conducted at 420 °C for 3 h. [c]Incineration was conducted at 650 °C for 3 h.

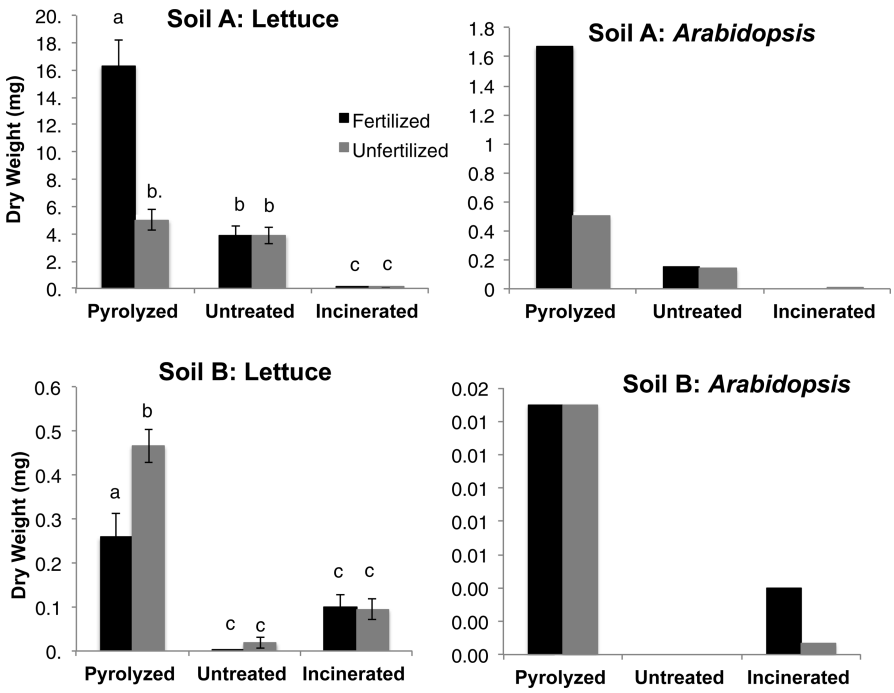

Figure 3. Mean plant dry weight after 21 days of growth. Pyrolyzed soils produce significantly more biomass than do contaminated and incinerated soils. The letters above the bars indicate significant differences ($p < 0.05$) among treatments per the Tukey test. Error was not calculated for *Arabidopsis* seedlings because the dried plants were too fragile to be handled and weighed individually, and these plants were weighed in bulk by treatment type.

patterns of homogeneous oil pyrolysis are also observed for our contaminated soils.

Over the range of the typical pyrolysis temperatures tested, the weight loss rates peaked between 400 and 450 °C for both contaminated soils (Figure 1). Therefore, a temperature of 420 °C was selected for further pyrolysis tests.

GC−FID analysis of soils A and B after pyrolysis under nitrogen for 3h at 420 °C showed significant removal of hydrocarbons (Figure 2). The area under the chromatogram of pyrolyzed soil A (which is the measure of the amount of solvent-extractable hydrocarbons) showed a 99.6% reduction when compared to that of contaminated soil A. The corresponding reduction for pyrolyzed soil B was 95.0%. Soil B apparently contains some hydrocarbons that require temperatures higher than 420 °C for complete removal (Figure S2).

More importantly, the pyrolytic treatment reduced TPH in soil A from 16 000 mg/kg to below the detection limit of 4 mg/kg. Similarly, soil B experienced a significant reduction in TPH, from 19 000 mg/kg to 290 mg/kg. These residual TPH concentrations easily meet regulatory thresholds (commonly 1000−10 000 mg/kg for crude oil, depending on location).[68−72] The removal of TPH was due both to (a) thermal desorption of low-molecular-weight hydrocarbons at temperatures below 350 °C, and (b) thermal degradation of the remaining hydrocarbons at higher temperatures to form char (or coke). Because contaminated soil A contained more saturated and aromatic hydrocarbons (Figure S2), TGA shows that it exhibited higher weight losses than soil B between 100 and 350 °C.[73] About 80% of the total weight losses of soil A occurred in this range, whereas the corresponding fractional loss for soil B was 71% (Table 2). Also, pyrolyzed soil B contained six times more C than the uncontaminated soil and significantly less C than the contaminated soil (Table 2), indicating that pyrolysis produced a significant amount of "char" that was not solvent-extractable and, thus, not detectable by GC−FID analysis.

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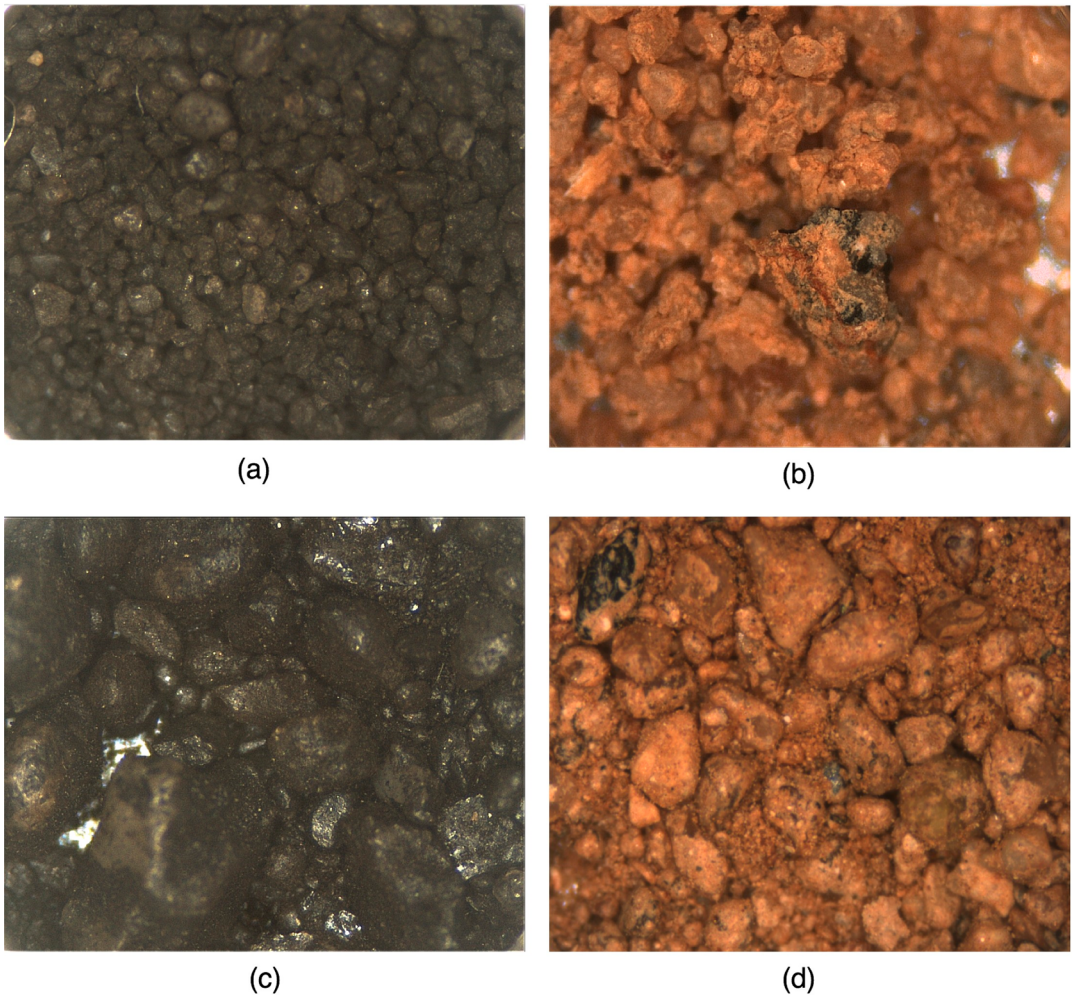

Figure 4. Optical microscopy of thermally treated soils. (a) Pyrolyzed soil A, (b) incinerated soil A, (c) pyrolyzed soil B, and (d) incinerated soil B.

Weight losses of uncontaminated soil B were less than 10% of those experienced by the contaminated soil (Table 2). This indicates that the majority of the dry-weight losses for contaminated soil B were due to hydrocarbon volatilization and degradation. Finally, weight losses measured after soils A and B had been pyrolyzed (3 h at 420 °C) or incinerated (3 h at 650 °C) were relatively small (Table 2), indicating that the selected pyrolysis conditions were appropriate.

Plant Growth Enhancement by Pyrolysis of Contaminated Soil. Both *Arabidopsis* and lettuce showed significantly higher germination and growth in pyrolyzed soils compared to incinerated or heavy hydrocarbon-contaminated soils, suggesting that soil pyrolysis may have a valuable niche in the soil remediation of weathered oil. In most cases, both *Arabidopsis* and lettuce seeds germinated sooner and in higher numbers in pyrolyzed soil than in contaminated or incinerated soil (Figures S3 and S4). In addition, both pyrolyzed soils allowed significantly more biomass production compared to contaminated or incinerated soils (Figure 3). Fertilization did not significantly affect germination or seedling mortality, but plants grown in pyrolyzed fertilized soil A were heavier than those that were not fertilized. Fertilization did not significantly improve seedling weight for pyrolyzed soil B. Although pyrolysis significantly enhanced soil fertility to facilitate regreening efforts, it may not fully restore soil fertility compared to (uncontaminated) soil. This is illustrated for uncontaminated soil B, which exhibited the highest germination and biomass yields (Figures S3c,d and S4c,d and Table S1).

Soil Pyrolysis without Significant Production of Polycyclic Aromatic Hydrocarbons. PAHs are potentially carcinogenic compounds that could be formed by the incomplete combustion of fossil fuels and biomass.[74] Preventing PAH formation and transport into groundwater is therefore of utmost importance. We measured the concentrations of the 16 EPA-designated priority PAHs in pyrolyzed soils and compared them to risk-based screening levels (RBSL) for Texas soils and PAH levels prior to treatment (Table S2). Most PAHs were below detection limits (0.003 mg/kg), with chrysene and phenanthrene being only slightly detectable at 0.004 mg/kg in soil A. Soil B had slightly higher PAH content, consistent with TGA and SARA results. Nevertheless, all PAHs in soil B were well below both RBSLs and common background level values for PAHs.[33] Results from the two soils analyzed here suggest no risk associated with PAH formation in soil pyrolysis.[27,33]

Pyrolysis without Considerable Effect on Agronomically Relevant Soil Properties. We hypothesized that by avoiding combustion, pyrolysis would be less destructive to soil fertility in comparison to incineration. Pyrolysis increased soil pH to a much lesser extent than incineration. Specifically, the pH increased from 7.2 to 8.4 for soil A and from 7.7 to 9.2 for

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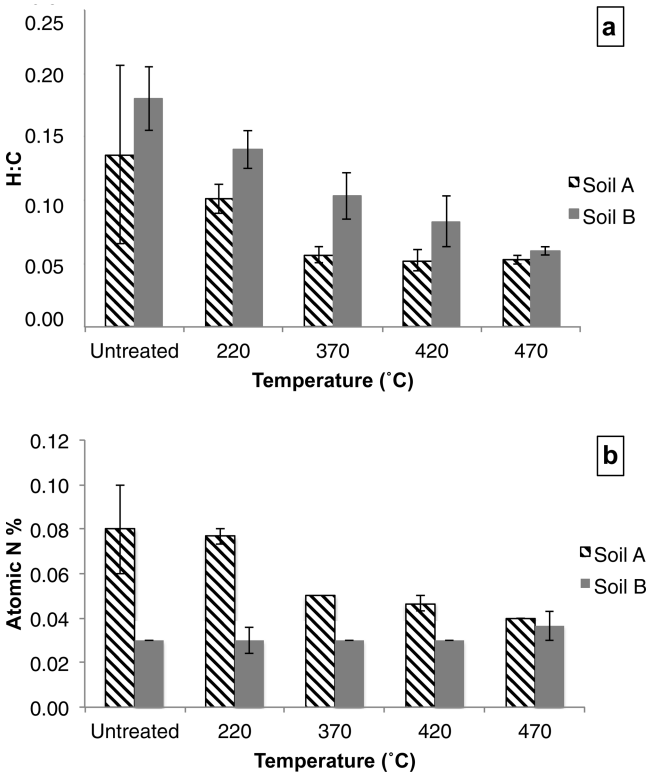

Figure 5. Elemental analysis of thermally treated soils. (a) The H:C ratio decreases with thermal treatment and increased pyrolysis temperature, consistent with char and coke formation. (b) Total N content varies for soil A but not for soil B with pyrolysis temperature.

soil B after pyrolysis (Table 1), whereas it increased to 11.1 (soil A) and 11.9 (soil B) following incineration.

Elemental analysis shows that the total soil-associated nitrogen was higher in pyrolyzed than in incinerated soils, with higher values corresponding to lower pyrolysis temperatures. Specifically, while NO_3−N values decreased more than 90% for all thermally treated soils, total Kjeldahl nitrogen (TKN) was retained to a greater extent in pyrolyzed soils (410−440 mg/kg)[75] compared to that in incinerated soils (40−60 mg/kg). Nitrogen losses are also observed in biochar production.[75] Typical nitrogen emissions from the pyrolysis of biomass (where nitrogen is primarily bound in proteins and low concentrations of plant nitrates) occur as HCN, NH_3, and HNCO, as well as in low levels of NO_x.[76−80]

By removing hydrocarbons, thermal treatment decreased hydrophobicity for both soils (Table 1). The reduction of hydrophobicity contributes to the restoration of soil health, as hydrophobicity increases erosion and reduces infiltration rates, seed germination, and plant growth.[81−83] Although pyrolysis and incineration both transformed soil A from Class 7 (very hydrophobic) to Class 5 (very hydrophilic) material, pyrolysis at 420 °C did not reduce the hydrophobicity of soil B below Class 5 levels. Our results suggest that this soil contains hydrocarbons that may require temperatures higher than 420 °C for the more complete degradation necessary to further decrease hydrophobicity. Finally, changes in the water-holding capacity after thermal treatment were not statistically significant (0.36 ± 0.02 versus 0.33 ± 0.03 for soil A before and after pyrolysis, respectively, and 0.29 ± 0.05 and 0.27 ± 0.04 for soil B) (Table 1). Maintenance of water-holding capacity is critical for healthy plant growth in the revegetation of remediated sites.

Although additional testing of different soils is necessary for the further substantiation of these trends, they suggest that soil pyrolysis may be a less destructive thermal-treatment option than incineration in regards to soil fertility.

Elemental Analysis and Microscopy Suggestion of Pyrolyzed Organic Carbon Deposition as a Thin Film. Elemental analysis (EA) of C and H content in soils before pyrolytic treatment and incineration showed that pyrolyzed soils retained organic carbon that is otherwise lost upon incineration. Incinerated soils contained very little carbon (0.32 ± 0.11 and 0.46 ± 0.11 wt %, respectively, for soil A and soil B), representing less than 1/10th of the C detected in the contaminated soils.[84] No hydrogen was detected in incinerated soils. EA analysis of contaminated soils showed H:C ratios of 1.62 for soil A and 1.95 for soil B (Figure 4), which are typical for heavy crudes.[55] As pyrolysis temperature increased, H:C decreased to less than 1, which is standard for petroleum cokes.[60] This decrease is due to the loss of hydrogen that occurs during the pyrolysis reactions that form characteristic clusters of aromatic rings.

Our data suggest that the char-like material coated the surface of pyrolyzed soil particles. This material has a similar composition to that of petroleum coke, based on the low H:C ratios observed for soils pyrolyzed at temperatures higher than 420 °C and the stark color differences (dark gray versus light brown) observed in images of pyrolyzed and incinerated soils (Figure 5). Note that in contrast to biochar production, the deposition of this material as a thin film on pyrolyzed soil particles should not change soil porosity or particle size.[85,86] Therefore, pyrolysis of hydrocarbon-contaminated soil is unlikely to trigger significant changes in soil properties such as water-holding capacity, plant-available water, and hydraulic conductivity, as can occur in biochar-amended soils.[51,85]

In summary, thermal treatment of soils impacted by weathered oil spills offers the ability to quickly remove recalcitrant high-molecular-weight hydrocarbons. Pyrolysis requires less energy and, for the two soils examined here, achieved near-total TPH removal while preserving important agronomic properties such as residual soil organic carbon and pH. We also observed increased biomass yields compared to those of plants grown in incinerated soils. Microscopy and elemental analysis suggest that pyrolysis leads to the formation of carbonaceous material (char) that coats the surface of soil particles. This represents an advantage over incineration, which burns not only contaminants but also natural organic matter that could be important for soil health. Therefore, pyrolysis has the potential to fill an important niche in the remediation of weathered hydrocarbons while also restoring soil fertility and enhancing revegetation.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.est.5b02620.

Figures showing the waste trap for the pyrolysis reactor, SARA analysis results, percentages of surviving lettuce and *Arabidopsis* seedlings. Tables showing the average dry weights of lettuce and *Arabidopsis* and PAH analysis results (PDF)

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Notes

The authors declare no competing financial interest.

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