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Pilot-Scale Pyrolytic Remediation of Crude-Oil-Contaminated Soil in a Continuously-Fed Reactor: Treatment Intensity Trade-Offs

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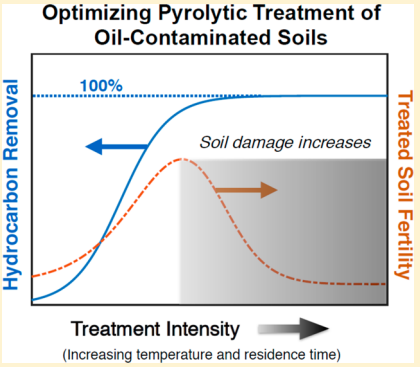
Supporting Information

ABSTRACT: Pyrolytic treatment offers the potential for the rapid remediation of contaminated soils. However, soil fertility restoration can be highly variable, underscoring the need to understand how treatment conditions affect soil detoxification and the ability to support plant growth. We report here the first pilot-scale study of pyrolytic remediation of crude-oil-contaminated soil using a continuously fed rotary kiln reactor. Treatment at 420 °C with only 15 min of residence time resulted in high removal efficiencies for both total petroleum hydrocarbons (TPH) (99.9%) and polycyclic aromatic hydrocarbons (PAHs) (94.5%) and restored fertility to clean soil levels (i.e., *Lactuca sativa* biomass dry weight yield after 21 days increased from 3.0 ± 0.3 mg for contaminated soil to 8.8 ± 1.1 mg for treated soil, which is similar to 9.0 ± 0.7 mg for uncontaminated soil). Viability assays with a human bronchial epithelial cell line showed that pyrolytic treatment effectively achieved detoxification of contaminated soil extracts. As expected, TPH and PAH removal efficiencies increased with increasing treatment intensity (i.e., higher temperatures and longer residence times). However, higher treatment intensities decreased soil fertility, suggesting that there is an optimal system-specific intensity for fertility restoration. Overall, this study highlights trade-offs between pyrolytic treatment intensity, hydrocarbon removal efficiency, and fertility restoration while informing the design, optimization, and operation of large-scale pyrolytic systems to efficiently remediate crude-oil-contaminated soils.



INTRODUCTION

Accidental and incidental oil spills are a common occurrence in terrestrial environments. Since 2010, more than 1300 oil spills[1] (totaling 9 000 000 gallons) occurred in the United States. Although marine spills are often highly publicized, the prevalence of land-based petroleum transport and storage make terrestrial spills more common.[2−5] Current remediation methods are either relatively slow or have unintended consequences in the form of soil damage and high energy usage.[6−13] Furthermore, some treatment processes such as aerobic bioremediation could activate toxic hydrocarbons and transform them to more-noxious byproducts such as PAH derivatives,[14] raising the possibility of meeting regulatory cleanup goals without achieving full soil detoxification. Therefore, there is a pressing need for the more-efficient and sustainable remediation of oil-contaminated soils.[15]

Pyrolysis is receiving increasing attention as an on-site remediation approach because of its potential to rapidly and reliably remove TPH with lower energy requirements and better post-treatment soil fertility than other ex situ thermal remediation approaches.[16] For example, compared to incineration at 600−1200 °C (which destroys soil fertility), pyrolytic treatment conducted at or below 500 °C has been shown to remove TPH from soils nearly completely without significant fertility damage.[17] However, soil fertility restoration is not consistently achieved by thermal treatment,[15,16,18−20] underscoring the need for mechanistic insight into how treatment conditions affect soil detoxification and ability to support plant growth.

Initial studies on pyrolytic treatment focused on small-scale batch tests to assess TPH removal and soil fertility restoration

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as well to understand the fundamental reaction mechanisms behind these outcomes.[16,17] After the desorption of light hydrocarbons between 150 and 350 °C, pyrolysis reactions dominate in the range of 400−500 °C, releasing gaseous products and forming a solid char.[16] Plant growth studies showed favorable soil fertility metrics in soils that were pyrolyzed at 420 °C for 3 h, suggesting the potential for improved ecosystem restoration following remediation compared to traditional thermal technologies.[17] Oil recovery has also been demonstrated during pyrolytic remediation (50.9% of carbon recovered following pyrolysis at 500 °C for 30 min in a small batch reactor), suggesting an additional potential benefit of pyrolysis over combustion-based thermal technologies.[21] While such laboratory-scale experiments were instrumental in demonstrating the proof of concept for pyrolysis and in informing process design, pilot-scale studies are needed to delineate the merits and limitations of pursuing multiple treatment objectives (e.g., TPH removal compliance, soil detoxification, and fertility restoration) as a function of pyrolysis conditions (e.g., temperature, soil residence time, and soil oil content). Ensuring reliable remediation also requires special attention to residual PAHs in the treated soil or its leachate because these priority pollutants are not only present in crude oil but also could be formed during thermal treatment.[22−24]

Here, we report the first pilot-scale study of pyrolytic soil treatment performed under continuously fed conditions to discern how treatment conditions affect not only TPH and PAH removal efficiency but also detoxification efficacy and the ability to support plant growth. A pair of contaminated soils were pyrolyzed in a continuously fed rotary kiln reactor at 370−470 °C for 15−60 min. TPH and PAH concentrations and key agronomic parameters of the treated soils were measured for each set of operating conditions. To quantify the effectiveness of pyrolysis in reducing potential toxicity to humans (e.g., through the inhalation of contaminated dust or the ingestion of impacted groundwater), the cytotoxicity of soil extracts was tested by the MTT colorimetric assay with a human bronchial epithelial cell line (BEAS-2B).[25−27] Plant growth studies were also conducted to characterize potential trade-offs between pyrolytic treatment intensity, remediation efficiency, and soil fertility restoration.

MATERIALS AND METHODS

Clean and Contaminated Soil Samples. Clean soil (background soil) was collected from Hearne, TX. The soil was a kaolinitic, sandy, clay loam (approximately 25% clay content) from the B horizon. After the soil was dried, homogenized, and sieved to remove large particles, the clean background soil was blended with a heavy crude oil (API 21°, Chevron, Houston, TX) to prepare two contaminated soil samples with oil concentrations of 3% and 5% by weight. These are representative concentrations for terrestrial oil spills. The total petroleum hydrocarbon (TPH) content of the contaminated soils was 14 000 and 18 000 mg/kg, respectively.

Pilot-Scale Continuous Short-Contact-Time Pyrolysis. Pilot-scale pyrolysis experiments were performed with a continuously fed rotary kiln reactor operated by Hazen Research (Golden, CO). The 7 in. diameter rotary kiln had 4 24 in. long electrically heated zones that were independently controlled to achieve the desired temperature profile (Figure 1). The kiln was insulated to minimize heat losses, and the power to the four electrical heaters was adjusted to (a) raise the temperature of the soil to the desired pyrolysis temperature in zone 1 (Figure 1) and (b) maintain zones 2 through 4 (Figure 1) at the same pyrolysis temperature for the target solid feed rate. For the purpose of this study, the solids residence time was the time the solids were exposed to the pyrolysis temperature in zones 2−4. Soil was fed with an adjustable speed screw feeder, and pure N_2 in a counter-current flow was used to "sweep" the desorbing hydrocarbons and pyrolysis products. The off-gas passed first through a cyclone to remove the fines and then through two tube-and-shell condensers to collect the condensable hydrocarbons. The pilot system is equipped with a computerized data acquisition system that monitors all process variables (temperatures, flows, pressures, off gas concentrations, etc.) at 30 s intervals.

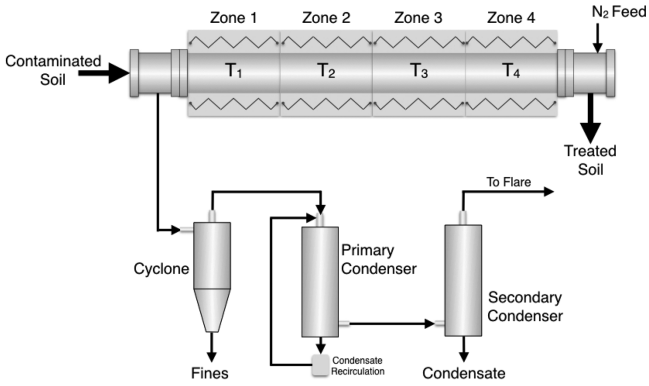

Figure 1. Schematic of the indirectly heated continuous kiln reactor for the fast pyrolysis of oil-contaminated soils showing the four independently controlled, electrically heated zones and the post-processing equipment.

A total of 15 pyrolysis experiments were carried out to investigate how key operating conditions (reactor temperature and solids residence time) affect (a) the efficacy of pyrolysis in reducing TPH and PAHs, (b) the detoxification of contaminated soils (assessed per toxicity to human cells), and (c) the treated soil fertility. The parameters studied were: oil content of contaminated soils (3 and 5 wt %); soil moisture (10 and 15 wt %); pyrolysis temperature (370, 420, and 470 °C); and residence time (15, 30, and 60 min). Using previous findings on the mechanisms of soil pyrolysis as guidance,[16] we narrowed the experimental matrix to the 15 runs shown on Table 1. Reactor operation details are provided in Figure S1. Briefly, the amount of contaminated soil processed with this pilot reactor ranged from 28 lb/h for a residence time of 15 min down to 7 lb/h when the kiln rotation speed was adjusted to maintain a residence time of 60 min.

All treated soils were analyzed for TPH and PAH content. Soil collected from 4 pyrolysis runs (nos. 6, 10, 13, and 14) was used for the plant growth studies and detoxification assessments described later in this paper.

TPH and PAH Measurements. TPHs and PAHs were measured by Lancaster Laboratories (Lancaster, PA, Tables 1 and 2). The TPH concentration was determined by measuring the solvent-extractable hydrocarbons via gas chromatograph−flame ionization detector based on U.S. Environmental Protection Agency (EPA) method no. 8015M. In addition, the 16 U.S. EPA priority pollutant PAH compounds were analyzed by EPA method no. 8270C (SW-846).

MTT Assay. This colorimetric cell viability assay quantifies NADH-dependent cellular oxidoreductase enzymes activity by

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Table 1. Pyrolytic Treatment Conditions

sample	pyrolysis temperature (°C)	residence time (min)	initial oil content (%)	initial moisture content (%)	residual TPH (mg/kg)
run no. 1[a]	420	30	0	10	12
run no. 2	470	30	0	15	<12
run no. 3	370	15	3	10	530
run no. 4	370	30	3	10	1100
run no. 5	370	60	3	10	27
run no. 6	420	15	3	10	15
run no. 7	420	30	3	10	<12
run no. 8	420	30	3	15	<12
run no. 9	470	15	3	15	<12
run no. 10	470	30	3	15	<12
run no. 11	370	30	5	10	380
run no. 12	420	15	5	10	<12
run no. 13	420	30	5	10	13
run no. 14	470	15	5	15	<12
run no. 15	470	30	5	15	30

[a]Pyrolysis run nos. 1 and 2 were controls with uncontaminated soil. Run nos. 3−10 were conducted with contaminated soil 1, containing 3% initial oil content, 10% initial moisture content, and 14 000 mg/kg TPH. Run nos. 11−15 were conducted with contaminated soil 2 containing 5% initial oil content, 10% initial moisture content, and 18 000 mg/kg TPH.

reducing the tetrazolium dye MTT [i.e., 3-(4,5-dimethylthiazol-2-yl)-2,5-diphenyltetrazolium bromide] to its insoluble formazan, which has a purple color.[28] We used this assay and a human bronchial epithelial cell line to test the detoxification of soils treated by pyrolysis.

Briefly, BEAS-2B, adenovirus 12-SV40 transformed normal human bronchial epithelial cells (non-Clara cell type), and an MTT cell proliferation assay kit were purchased from ATCC (Manassas, VA). RPMI 1640 medium and dimethyl sulfoxide (DMSO) were purchased from Sigma-Aldrich. Samples (500 g each) of clean soil, 3% oil contaminated soil, and 4 pyrolyzed soils (runs nos. 6, 10, 13, and 14; Table 1) were extracted with 600 mL of 1:1 acetone/hexane by orbital shaking at 250 rpm at 37 °C. The extracts were concentrated to 20 mL by blowing with compressed air in chemical hood.[29,30] The MTT assay was performed in a 96-well plate. A total of 10 000 cells were plated in 100 μL of culture medium in each test well (4 wells per leachate sample) and kept at 37 °C overnight. The following day, 1 μL of concentrated leachate sample containing the extract from 1.25 mg of soil (or 1 μL of DMSO as negative control) was added in each well, and the plate was incubated at 37 °C for 48 h. MTT reagent (10 μL) was then added to each test well and incubated for 2 h until a purple precipitate was visible. Thereafter, 100 μL of detergent reagent was added to each test well, and the plate was kept at room temperature in the dark for 2 h. Cell viability was represented by absorbance at 570 nm,[31] measured with a fluorescence plate reader (SpectraMax GeminiXS).

Soil Fertility and Plant Growth Studies. The pyrolyzed soils were tested for agronomically relevant properties by the Texas A&M Soil, Water, and Forage Testing Laboratory (Table 3). We grew *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. Lettuce has been identified as a valuable plant for hydrocarbon-contaminated soil testing due to high sensitivity to petroleum toxicity.[32] The pyrolyzed soils had large aggregates (approximately 2−6 cm) following treatment that were broken with a mortar and pestle. The smaller particles were sieved so that the final soil had aggregates between 0.5 and 2.0 mm. These soil samples were mixed, moistened, and packed into 50 mL pots with filter paper at the bottom to prevent excess soil loss. A total of 5 replicates (5 pots) were used for each soil type and 10 seeds were planted in each pot. Half of the treatments were fertilized with quarter-strength Hoagland's solution to assess the benefits of nutrient addition to pyrolyzed soil fertility. The other half of the soils was treated with water and served as the control group. 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 were monitored for 21 days. After harvesting, we measured the root length of each plant and dried the plants for 48 h at 65 °C. The dry weight of the plants was then recorded to measure total biomass production.

Table 2. Concentrations of the 16 EPA-Regulated PAHs in Different Soil Samples (Micrograms per Kilogram)

	clean soil	contaminated soil 1	contaminated soil 2	no. 6	no. 10	no. 13	no. 14
acenaphthene	BDL[a]	BDL	540	10	BDL	BDL	BDL
acenaphthylene	11	BDL	BDL	4	12	BDL	BDL
anthracene	6	BDL	BDL	11	6	4	BDL
benzo(a)anthracene	BDL	350	940	21	BDL	7	4
benzo(a)pyrene	11	120	480	8	9	BDL	BDL
benzo(b)fluoranthene	14	280	630	13	13	5	BDL
benzo(g,h,i)perylene	13	270	420	12	9	5	4
benzo(k)fluoranthene	6	BDL	67	4	5	BDL	BDL
chrysene	BDL	3800	6300	39	5	9	6
dibenz(a,h)anthracene	BDL	190	390	9	BDL	4	BDL
fluoranthene	BDL	240	610	17	BDL	6	7
fluorene	BDL	BDL	1300	28	BDL	7	4
indeno(1,2,3-cd)pyrene	BDL	BDL	120	11	8	4	BDL
naphthalene	BDL	89	2000	64	5	18	15
phenanthrene	BDL	BDL	1500	99	17	20	32
pyrene	BDL	1400	2500	20	BDL	7	6
Total	**69**	**6739**	**17 797**	**370**	**89**	**96**	**78**

[a]BDL: below detection limit (~3 μg/kg).

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Table 3. Agricultural Characteristics of Treated (Pyrolyzed) Soils

	pH	conductivity (umho/cm)	nitrate N (ppm)	phosphorus (ppm)	potassium (ppm)	calcium (ppm)	magnesium (ppm)	sulfur (ppm)	sodium (ppm)
clean/uncontaminated	4.9	95	1	1	87	591	323	19	36
contaminated (3% Oil)	6.1	78	0	1	48	402	212	10	23
run no. 1	5.4	109	1	13	203	412	86	23	23
run no. 2	5.2	88	0	15	143	234	67	20	9
run no. 3	5	88	0	5	116	329	107	15	24
run no. 4	5.1	103	0	6	129	323	93	17	23
run no. 5	5.1	103	0	7	148	282	82	20	22
run no. 6	5	98	0	8	167	261	78	21	22
run no. 7	5.1	86	1	10	152	228	64	23	18
run no. 8	5.1	86	0	9	137	234	65	21	17
run no. 9	5	80	0	11	106	172	55	20	10
run no. 10	4.9	103	0	11	81	150	45	19	6
run no. 11	5.2	82	0	5	103	283	77	14	21
run no. 12	5.1	103	0	8	195	261	67	21	22
run no. 13	5.1	93	0	9	157	246	64	22	22
run no. 14	5	83	0	12	89	242	52	21	8
run no. 15	5.1	102	0	8	155	273	75	20	22

The preparation of quarter-strength Hoagland's solution[33] (fertilizer) is summarized in Table S1. All of the chemicals used in this study were purchased from Sigma-Aldrich Corporation. Deionized water was used in all experiments.

Statistical analysis. All statistical analyses were performed using SPSS 11.0 software and Microsoft Excel 2016. First, the data were analyzed for homogeneity of variance (Levene's test). Then, the significant differences between group means were determined by the *t* test at the 95% confidence level.

RESULTS AND DISCUSSION

Effective TPH and PAH Removal Achieved at 420 °C within 15 min. *TPH Removal.* Accounting for 2 important variables in contaminated soils, we carried out pyrolytic treatment experiments with 2 oil contents (3 and 5 wt %) and 2 different moisture contents (10 and 15 wt %). Table 1 shows the properties of the feed, the operating conditions of the pyrolysis reactor, and initial and residual TPH concentrations for all 15 pyrolysis runs. Approximately 99.9% TPH removal was achieved when soil contaminated with 3 wt % oil was treated at 420 °C for 15 min (pyrolysis run no. 6). Near complete TPH removal was also observed when pyrolysis was carried out at 420 °C for 30 min or at 470 °C for 15 or 30 min. Pyrolysis at 420 or 470 °C was also very effective in removing TPH from contaminated soils with 5 wt % oil content. TPH removal for these treated soils (pyrolysis run nos. 11−15) was over 99.8%. Significant TPH removal was also observed at 370 °C, with 96.2%, 92.1%, and 99.8% removal achieved with pyrolysis times of 15, 30, and 60 min, respectively (pyrolysis run nos. 3−5).

These results corroborate previous work[16,17,21] showing that regulatory TPH compliance can be achieved with relatively mild pyrolytic treatment conditions. High TPH removal efficiency was achieved at 370 °C, indicating that (depending also on the composition of the contaminating oil) pyrolytic treatment can reliably meet common TPH regulatory limits (<0.1% by operating weight) by treating crude-oil contaminated soils at temperatures below 420 °C and using adequate solid residence time. The demonstrated ability to completely remove TPH at 420 °C with 15−30 min soil residence time highlights the potential for energy savings when pyrolysis is compared with thermal methods operating at significantly higher temperatures.[17,34] However, thermal treatment methods that use direct-fired kilns may benefit by the energy released when oil hydrocarbons are combusted with air. Thus, a detailed analysis with process simulators is necessary to provide an accurate comparison of energy requirements.

PAH Removal. Polycyclic aromatic hydrocarbons are ubiquitous environmental pollutants that have been linked to skin, lung, and bladder cancer in humans as well as to poor fetal development.[14,22,35,36] The U.S. EPA has identified 16 PAHs as priority pollutants.[37] Accordingly, we measured the concentrations of these 16 PAHs in the background (clean) soil, the 2 contaminated soils (3 and 5 wt %), and 4 of the treated soils (run nos. 6, 10, 13, and 14) that had been pyrolyzed at different temperatures and residence times.

Pyrolytic treatment reduced PAH concentrations in all samples, including the sample treated at the lowest temperature/time (420 °C, 15 min), which exhibited a 94.5% removal efficiency (run no. 6 in Table 2). PAH removal efficiencies exceeded 98.6% when either the residence time increased to 30 min or the pyrolysis temperature was raised to 470 °C, even when the initial concentration of oil in the contaminated soil was 5 wt %. For this particular oil/soil system at least, pyrolysis at 420 °C for 30 min or 470 °C for 15 min was effective in reducing the total concentrations of the 16 priority PAHs to levels that were statistically undistinguishable ($p > 0.05$) from clean (background) soil.

Pyrolytic Remediation and Significant Decrease of Soil Toxicity. The ability of pyrolytic treatment to detoxify contaminated soils was tested using human lung cells, a common model for assessing the impact of potential toxicants on cell metabolic activity and cell viability.[38] Figure 2 shows that the extract from crude-oil-contaminated soil was toxic to human lung cells because it significantly decreased their viability.[39] However, pyrolytic treatment resulted in effective detoxification, with increasing metabolic activity observed for cells exposed to extract from soil treated at higher pyrolysis temperatures. This underscores the need for adequate pyrolytic treatment intensity to not only remove TPH but also minimize potential health risks associated with specific organic toxicants such as residual PAHs and their potentially more toxic

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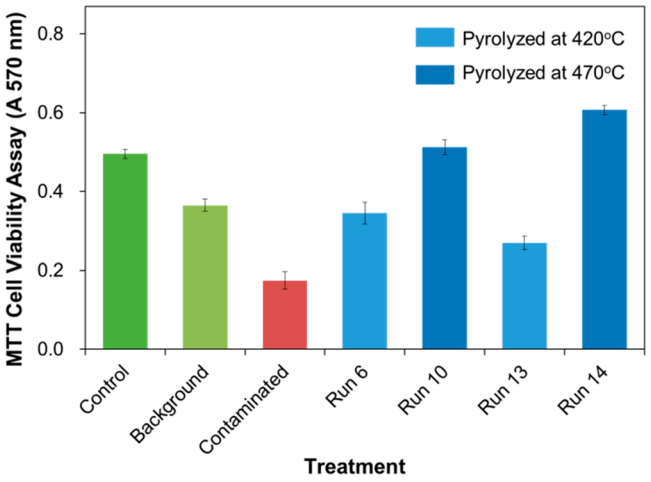

Figure 2. Pyrolytic treatment detoxified contaminated soils with different oil and moisture contents. The contaminated soil tested contained 3 wt % oil, its moisture content was not adjusted, and the control consisted of DMSO reagent without soil extract. The initial and treatment conditions for the other soils are listed below. Run 6: Contaminated soil with 3 wt % oil and 10 wt % moisture was pyrolyzed at 420 °C with a 15 min residence time. Run 10: Contaminated soil with 3 wt % oil and 15 wt % moisture was pyrolyzed at 470 °C with a 30 min residence time. Run 13: Contaminated soil with 5 wt % oil and 10 wt % moisture was pyrolyzed at 420 °C with a 30 min residence time. Run 14: Contaminated soil with 5 wt % oil and 15 wt % moisture was pyrolyzed at 470 °C with a 15 min residence time. Error bars depict plus or minus one standard deviation (SD) from the mean of four replicates.

byproducts of aerobic transformations.[14] While temperature is the dominant factor in determining the intensity of pyrolytic treatment,[40] three additional parameters (soil oil content, soil moisture content, and residence time) vary among the soils depicted in Figure 2 and may contribute to the observed response variability. An additional source of variability may be that the reactor temperature occasionally deviated by more than ±5 °C from the target (set point) pyrolysis temperature of 420 or 470 °C (see Figure S2). Overall, however, Figure 2 shows that this continuously fed, pilot-scale (anoxic) pyrolytic process was very effective in detoxifying contaminated soils with different oil contents.

Pyrolyzed Soil and Exhibition of High Fertility Restoration. Most soil agricultural characteristics were similar after pyrolytic treatments to those of uncontaminated soil (Table 3). For example, pH ranged from 4.9 to 5.4 for pyrolyzed soils compared to 4.9 for uncontaminated background soil. To further assess the regreening potential of pyrolyzed soil, we grew *Lactuca sativa* in background (clean) soil, 3% oil contaminated soil, and pyrolyzed soils (no. 13 soil) for 21 days.

Germination studies alone were not sufficient to assess soil fertility restoration by pyrolytic treatment. Plants grown in pyrolyzed soil with fertilizer showed lower germination rates after 7 days than plants grown in clean soil (Figure 3a), which may have resulted from limited oxygen availability caused by partial soil hardening.[41] After 21 days, however, plants grown in pyrolyzed soil with fertilizer exhibited the same germination rates as plants grown in clean soil. A similar germination trend of watered plants (without fertilizer) grown in pyrolyzed soil was also observed (Figure 3b). In contrast, plants grown in contaminated soil showed poor survival despite amendments. Interestingly, contaminated soils initially showed a positive germination trend, perhaps because of improved water and air transport due to large, oily "clumps".[42]

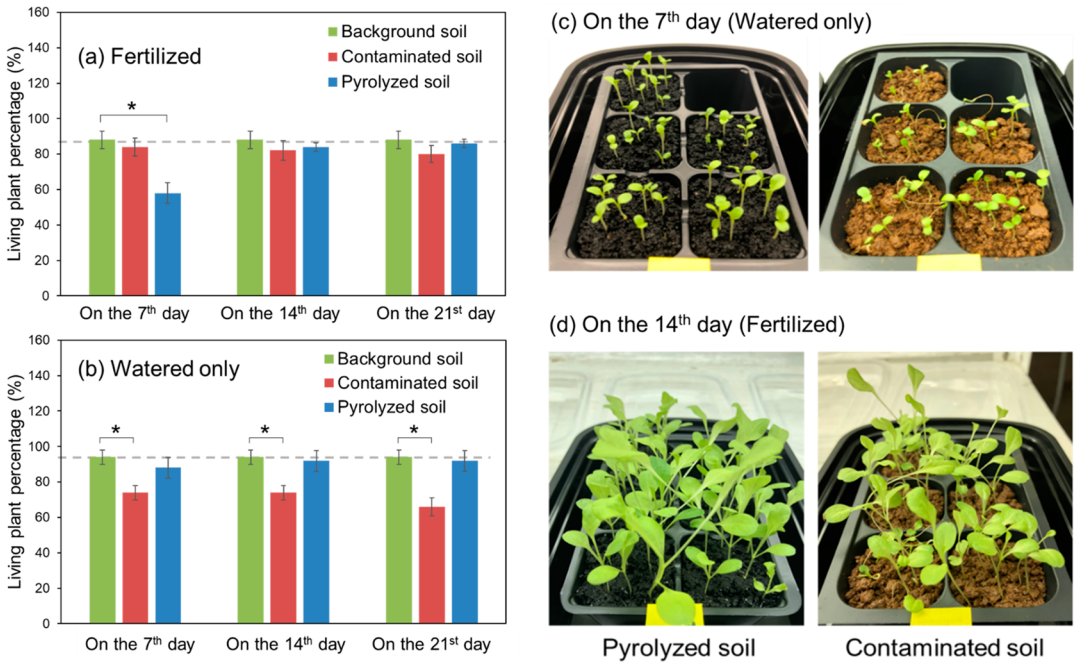

Figure 3. Germination trends presented as percentage of live plants (relative to number of seeds planted) on the 7th, 14th, and 21st day (panel a: fertilized; panel b: watered only). Lettuce growth in different soils after (c) 7 and (d) 14 days. Data are shown as mean plus or minus SD, $n = 5$. Contaminated soil: 3% oil soil; pyrolyzed soil: soil with 5% oil was treated at 420 °C for 30 min; soil aggregates: 0.5−2.0 mm. Asterisks denote a significant difference in comparison to the background group at the 95% confidence level; single asterisks indicate $p < 0.05$ (independent samples t test)

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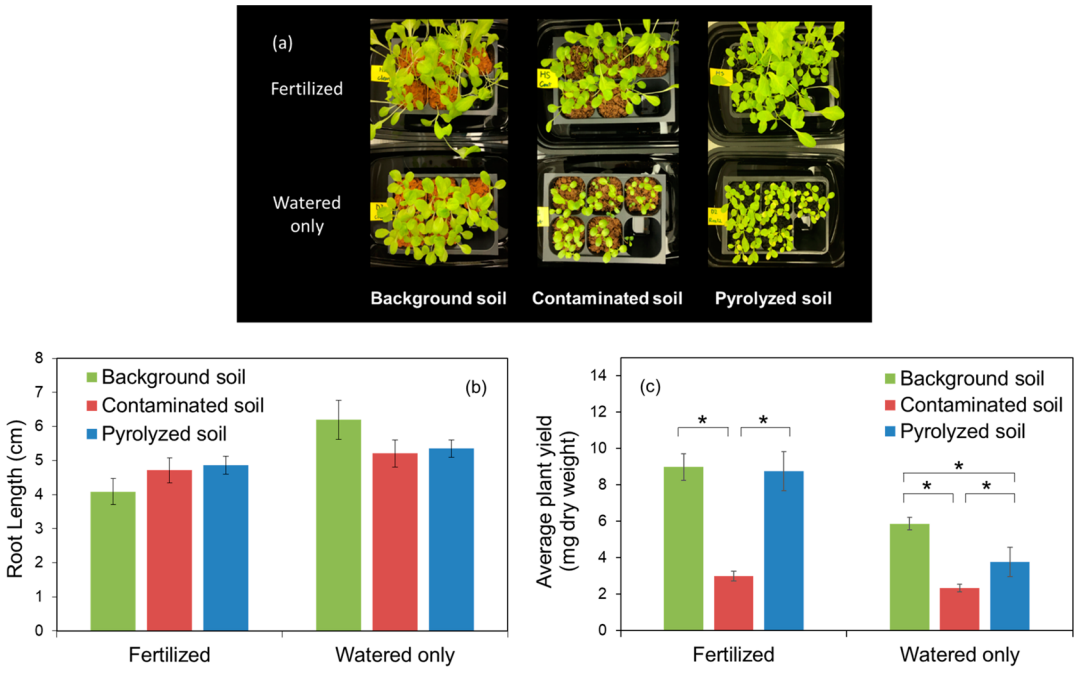

Figure 4. Fertility enhancement by pyrolytic treatment. (a) Photograph of lettuce in different soils on the 21st day. (b) Average root length for lettuce plants grown in different soils after 21 days. (c) Average plant weight for lettuce plants grown in different soils after 21 days. Data were shown as mean plus or minus SD, n = 45. Contaminated soil: 3% oil soil; pyrolyzed soil: soil with 5% oil was treated at 420 °C for 30 min; pyrolyzed soil aggregates: 0.5−2.0 mm. The root lengths of contaminated soil and pyrolyzed soil were statistically similar to background soil at the 95% confidence level. Asterisks denote a significant difference in comparison with the background group or contaminated soil at the 95% confidence level; single asterisks indicate $p < 0.05$; independent samples t test.

Pyrolytic treatment improved the size, weight, and visually assessed (morphological) health of plants during the first 14 days. Because of the toxicity of crude oil and the hydrophobicity of oily soils and despite the relatively high germination percentage, seedlings growing in contaminated soil often displayed signs of poor health, such as very long, thin, yellow, curving stems, culminating in plant death or abnormal morphology (Figure 3c,d). This is in agreement with previous work showing that germination studies alone are not sufficient to predict the ability of thermally treated soils to support plant growth and ecosystem restoration.[17] Thus, medium- and long-term studies are necessary to assess the regreening potential of soils; in this study, 7 day germination rates would have led to the erroneous conclusion that plants grow better in contaminated soils.

Pyrolytic treatment significantly enhanced plant growth relative to contaminated soils. Despite initial similarities in seed germination, pyrolyzed soils produced larger and healthier looking plants than contaminated soils by the 21st day of the growth tests (Figure 4a). Improved outcomes for pyrolyzed soils were also seen in the root lengths after the 21 day growth period (Figure 4b). The "root-to-shoot" ratio is a well-established phenomenon in plant biology,[43,44] with multiple studies finding that nutrient and water deficiencies in the soil can lead plants to grow longer roots. As expected, the roots of plants in unfertilized soil were significantly longer than those soils with fertilizer. Because the pyrolyzed soils were kept moist and the fertilized plants displayed much-shorter root systems, it is likely that nutrient deficiencies caused this behavior. In the same culture condition (water or fertilizer), moreover, there were no statistically significant differences among the root lengths of plants grown in clean, contaminated, and pyrolyzed soils, suggesting that the plant root length was not inhibited by petroleum contamination.

Importantly, plant growth was significantly enhanced by pyrolyzing contaminated soil (Figures 4c and S3). In some cases, soils pyrolyzed at 420 °C for 30 min allowed fertilized plants to reach the same average weight of plants grown in clean fertilized soil (8.8 ± 1.1 versus 9.0 ± 0.7 mg dry weight). Furthermore, fertilization resulted in a significant increase of the weight of plants grown in both clean soil and pyrolyzed soil, although the beneficial effect of fertilization was minimal for plants growing in contaminated soil. Therefore, our results indicate that pyrolytic remediation (especially when coupled with the addition of fertilizer) significantly improves the potential for vegetation restoration, which can stimulate seedling growth and plant development in the following period.

Optimal Treatment Intensity to Restore Soil Fertility, beyond Which Soil Damage Occurs. Whereas more intense thermal treatment is conducive to faster and more complete TPH and PAH removal, it may also destroy soil fertility. To balance efficient remediation and optimize fertility restoration of contaminated soils, the following plant experiments were conducted in 4 representative pyrolyzed soils (nos. 6, 10, 13, and 14) pyrolyzed at 420 and 470 °C for 15 or 30 min. As expected, crude-oil contaminated soil possessed a lower ability to support plant growth compared to clean soil (3.0 ± 0.3 versus 9.0 ± 0.7 mg dry weight; Figure 5a). In contrast, plants grown in all pyrolyzed soils had survival rates equal to those of clean soil (Figures 5b and S4). Furthermore, treatment at 420 °C for 30 min achieved similar plant biomass yield as uncontaminated soil (8.8 ± 1.1 mg dry weight; Figure 5a), demonstrating the potential for pyrolytic treatment to efficiently restore soil fertility.[17] Importantly, though, pyrolytic

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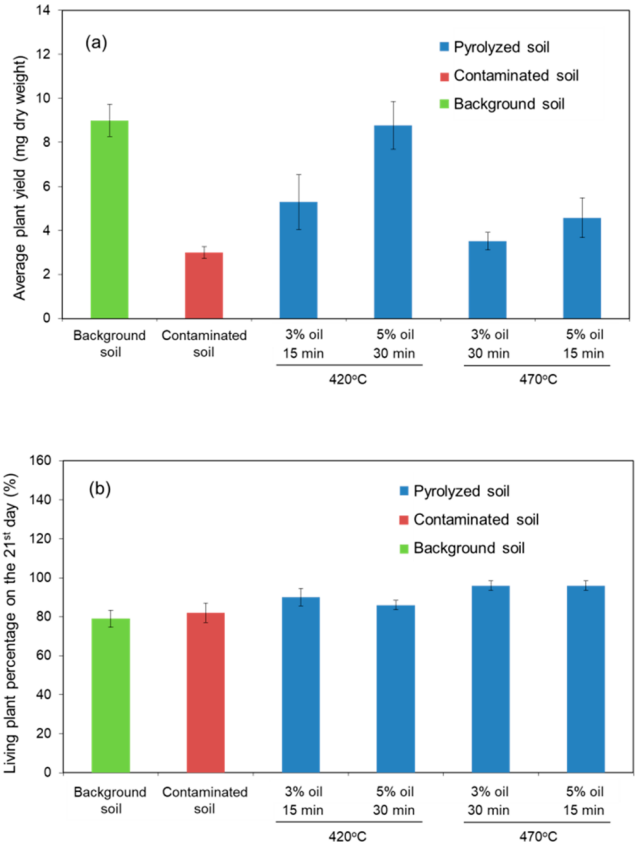

Figure 5. (a) Average plant weight and (b) percentage of live plants relative to number of seeds planted on the 21st day for lettuce plants grown with fertilizer in background soil (clean), contaminated 3% oil soil, and 4 pyrolyzed soils. Data were shown as mean plus or minus SD; n = (a) 5 and (b) 45.

treatment intensity (which increases linearly with the residence time of solids in the reactor and exponentially with the pyrolysis temperature)[40] affected plant growth patterns (Figure 6). For example, compared with the soils pyrolyzed at 420 °C, a higher pyrolysis temperature (470 °C) significantly reduced the average plant weight regardless of whether the plants were fertilized or not. Although TPH can be quickly removed at higher pyrolysis temperatures, system-specific optimization is essential to limit energy costs, soil damage, and ultimately, enhance plant biomass yields.[15,16]

There is a minimum pyrolytic treatment intensity needed to achieve regulatory TPH compliance and PAH removal. Whereas slightly higher treatment intensity may optimize soil fertility restoration (Figure 6), there is no benefit in exceeding this point. Longer pyrolysis residence time and higher temperatures would increase energy consumption and treatment cost while damaging soil fertility and reducing plant yields. This is illustrated by soils pyrolyzed at 470 °C for 15 versus 30 min; increased contact time decreased plant yields from 4.6 ± 0.9 to 3.5 ± 0.4 mg dry weight (Figure 5a). However, when treating this soil at a lower temperature (e.g., 420 °C), insufficient contact time (e.g., decreasing soil residence time from 30 to 15 min) may increase residual PAH concentrations (e.g., from 96 to 370 and μg/kg), which could inhibit plant growth[45,46] (Figure 5a, 5.3 ± 1.2 versus 8.8 ± 1.1 mg dry weight). Thus, an appropriate residence time for pyrolytic treatment should ensure effective soil detoxification.

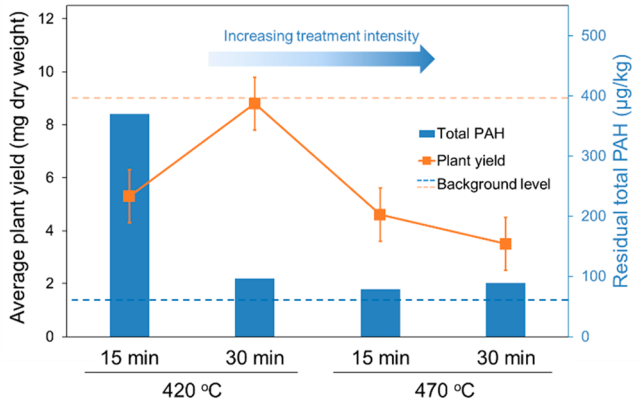

Figure 6. Multiple remediation objectives (e.g., regulatory cleanup compliance and soil fertility restoration) can be achieved with appropriate intensity of pyrolytic treatment that ensures efficient PAH removal (favored at higher intensity) without damaging soil fertility (concern for higher intensity). For this soil contaminated with 3−5% crude oil, TPH was removed efficiently (>99.9%) for all treatment conditions, and a pyrolysis temperature of 420 °C with a soil residence time of 30 min achieved both efficient PAH removal and restored ability to support the growth of *Lactuca sativa* to background (clean) soil levels.

Overall, this work shows that different treatment objectives (e.g., residual TPH and PAH compliance, detoxification, and soil fertility restoration) need not be mutually exclusive and could be simultaneously achieved by selecting appropriate pyrolytic treatment intensity (controlled through pyrolysis temperature and residence time). Whereas ensuring minimum treatment intensity is critical for reliable regulatory compliance, there is a maximum intensity beyond which pyrolytic treatment becomes detrimental with regards to both soil damage and excessive energy usage (Figure 6). Accordingly, there is a (system-specific) range of treatment intensities for which such trade-offs may be feasibly managed through appropriate pyrolytic treatment system design and operation.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.est.8b05825.

Additional soil properties and plant experiments data (PDF)

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Notes

The authors declare no competing financial interest.

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