

Effects of temperature and soil components on emissions from pyrolysis of pyrene-contaminated soil

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Abstract

Effects of temperature and soil on yields and identities of light gases (H_2 , CH_4 , C_2H_2 , C_2H_4 , C_2H_6 , CO , and CO_2) and polycyclic aromatic hydrocarbons (PAH) from thermal treatment of a pyrene-contaminated (5 wt%) soil in the absence of oxygen were determined for a U.S. EPA synthetic soil matrix prepared to proxy U.S. Superfund soils. Shallow piles (140–170 mg) of contaminated soil particles and as controls, neat (non-contaminated) soil (140–160 mg), neat pyrene (10–15 mg), neat sand (230 mg), and pyrene-contaminated sand (160 mg), were heated in a ceramic boat inside a 1.65 cm i.d. pyrex tube at temperatures from 500 to 1100 °C under an axial flow of helium. Volatile products spent 0.2–0.4 s at temperature before cooling. Light gases, PAH and a dichloromethane extract of the residue in the ceramic boat, were analyzed by gas chromatography or high pressure liquid chromatography (HPLC). Over 99% pyrene removal was observed when heating for a few tens of seconds in all investigated cases, i.e., at 500, 650, 750, 1000, and 1100 °C for soil, and 750 and 1000 °C for sand. However, each of these experiments gave significant yields (0.2–16 wt% of the initial pyrene) of other PAH, e.g., cyclopenta[cd]pyrene (CPP), which mutates bacterial cells and human cells in vitro. Heating pyrene-polluted soil gave pyrene conversions and yields of acetylene, CPP, and other PAH exceeding those predicted from similar, but separate heating of neat soil and neat pyrene. Up to 750 °C, recovered pyrene, other PAH, and light gases accounted for all or most of the initial pyrene whereas at 1000 and 1100 °C conversion to soot was significant. A kinetic analysis disentangled effects of soil–pyrene interactions and vapor phase pyrolysis of pyrene. Increase of residence time was found to be the main reason for the enhanced conversion of pyrene in the case of the presence of a solid soil or sand matrix. Light gas species released due to the thermal treatment, such as acetylene and methane, lead the formation of other, pyrene-derived PAH, e.g., methylpyrenes, cyclopenta[cd]pyrene, and benzo[a]pyrene. Implications of these findings for the chemistry of soil thermal decontamination and for diagnosing potential defects in soil thermal cleaning, e.g., incomplete elimination of targeted pollutants and formation of adverse by-products, are discussed.

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1. Introduction

Many physical, biological, and thermal processes for soil cleanup have been proposed with several demonstrated

at commercial scale. Thermal treatment provides soil decontamination efficiencies exceeding 99%. The required treatment times can range from a few seconds, to several tens of seconds, to multiple minutes, for treatment temperatures of ca. 750–1000, 400–600, and 150–300 °C, respectively [1,2]. Catalysts and exogenous reagents (e.g., O_2) shorten cleaning times or inhibit release of adverse by-products. To

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fulfill regulatory objectives, soil remediation technologies must eliminate targeted pollutants with high efficiencies without releasing unacceptable amounts of hazardous by-products to the ambient environment.

Several studies have investigated effects of temperature, heating rate, total pressure, pollutant type, and soil components [3–9]. Physical transport of pollutants away from individual soil particles and through packed soil beds have been simulated mathematically [2,3,5]. However, chemical reactions of contaminants during their separation from soil have typically not been fully accounted for in such simulations, even though such chemistries may give rise to adverse by-products, e.g., carcinogenic or mutagenic polycyclic aromatic hydrocarbons (PAH) [9]. For instance, evidence has been found that soil itself may contribute to the production of PAH with increased toxicity during thermal treatment of PAH-contaminated soil [9].

The objective of the present study was to elucidate how bioactive PAH are generated from a non-bioactive PAH contaminant during soil thermal treatment. Effects of temperature (500–1100 °C) and soil itself on the yields and identities of light gases (H₂, CH₄, C₂H₂, C₂H₄, C₂H₆, CO, and CO₂), and of pyrene, cyclopenta[*cd*]pyrene (CPP), and nine other polycyclic aromatic hydrocarbons (PAH) from controlled thermal treatment of a pyrene-contaminated soil were experimentally determined. Reactive gases, including O₂ were excluded from the apparatus to provide a benchmark for comparison with soil heating under reactive atmospheres. To assess the impact of heterogeneous catalytic effects in comparison to the presence of reactive species in the soil, control experiments with pyrene-contaminated sand have been conducted. Pyrene is a common by-product of fuel-rich combustion processes and often present in heavy oils, tars, and some sludges at U.S. hazardous waste sites [7]. Global kinetics parameters for three hypothesized pathways for pyrene destruction: vapor phase pyrolysis, catalysis by sand, and catalysis by or reaction with, soil or its decomposition products were investigated. Implications of the results for the chemistry of thermal soil decontamination and for detection of potential defects in soil thermal cleaning are discussed.

2. Methods and materials

The soil was a U.S. EPA synthetic soil matrix, free of anthropogenic contamination and prepared elsewhere to reflect attributes of soils encountered at U.S. Superfund sites [10,11]. This material has been also used in other studies of soil decontamination [7–12]. The elemental composition and the amounts of various minerals (sand, gravel, silt, top soil, and clays) blended to synthesize this soil have been reported previously [10–12]. It contains 0.38% of organic carbon some of which is believed to decompose to light gases during thermal treatment [12]. Rapid pyrolysis of this soil under 0.122 MPa of helium at 350–1050 °C led to the identification of H₂, CO, CO₂, CH₄, C₂H₆, C₂H₄, and C₂H₂ in the

volatile products but no light hydrocarbon exhibited yields of >0.1 wt% of soil [12].

The present study used a 63–125 μm size fraction of this soil, obtained by mechanical dry sieving. A 53–180 μm size fraction of sand was obtained by sieving Ottawa sand (EM Science). Pyrene (99%, Aldrich) served as an exogenous contaminant for both soil and sand. Analysis of this pyrene by high pressure liquid chromatography (HPLC) and gas chromatography coupled to mass spectrometry (GC/MS) detected at least two contaminants: 4H-cyclopenta[*def*]phenanthrene and at least one unidentified peak eluting from the GC column just before pyrene [9].

Before heating, neat soil samples were preconditioned by drying for 2 days over Drierite[®] (anhydrous calcium sulfate) in a dessicator. Soil to be contaminated was thus preconditioned, then contaminated (see below), and then redried in a dessicator for 2 days before heating. Pretreatment was found to stabilize soil moisture content to approximately 1 wt%. The soil was contaminated with pyrene using a procedure of Saito et al. [7,8]. An unbroken layer of about 5 g of soil was then covered with a concentrated solution of pyrene (about 45 g/L) in dichloromethane (DCM) and then sealed for 12 h to provide time for the soil to adsorb pyrene from the solvent. The solvent was then allowed to evaporate slowly over 8–10 h in an inverted wide mouth jar. The initial contamination level (CL₀), expressed as a percentage of soil (sand) plus contaminant was 4.8 ± 0.1 wt% (4.9 ± 0.1 wt%). The CL₀ was determined by assuming all the pyrene dissolved in the DCM was adsorbed by the substrate. The result for soil was confirmed by HPLC analysis of the amount of pyrene recovered by DCM extraction of a sample of contaminated soil.

Small batches (ca. 140–170 mg) of pyrene-contaminated soil and, as controls, neat (non-contaminated) soil (ca. 140–160 mg), neat pyrene (ca. 10–15 mg), neat sand (ca. 230 mg), or pyrene-contaminated sand (ca. 160 mg), were separately heated at one or more temperatures from 500 to 1100 °C. To exclude that the contamination procedure significantly effects soil behavior upon heating, a “pretreated neat soil”, i.e., a sample of soil subjected to the same procedure used to pollute it with exogenous pyrene but with the pyrene omitted, was heated at 1100 °C.

Specimens were heated in a ceramic boat contained within a quartz tube (80 cm long × 1.65 cm i.d.) horizontally mounted within a 32 cm long tubular electric furnace (Fig. 1). Throughout heating, a continuous flow of helium conveyed vaporized products from the boat to two downstream collection stations: first a cold finger (CF), i.e., a water-cooled glass tube for trapping less volatile products including pyrene and other PAH; and then a gas sampling bag (1 L Tedlar bags, Supelco) for capture of light gases as well as PAH not retained by the cold finger. The gas sampling bag was connected to the exit of the quartz tube just before the specimen was introduced to the furnace (see below) and was removed about 20–30 s thereafter. Assuming plug flow, the average residence time for volatiles between the boat and the cold finger was 0.2–0.4 s.

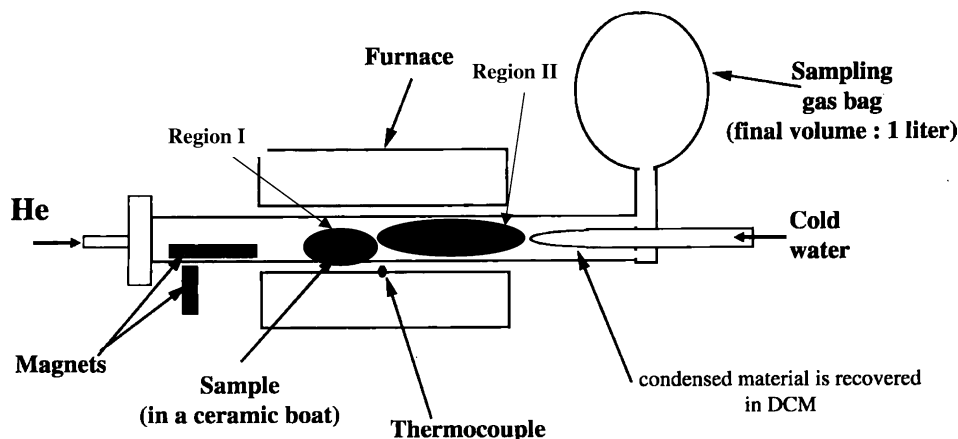


Fig. 1. Experimental setup.

The ceramic boat containing a known weight of sample was inserted into the quartz tube upstream of the furnace entrance while a continuous helium flow purged air from the tube. The furnace was preheated to 500, 650, 750, 1000, or 1100 °C (± 20 °C) measured with a type *K* thermocouple located within the furnace but outside the quartz tube. When the furnace reached the desired temperature, the ceramic boat was transferred into an axially isothermal high temperature region of the furnace (Region I, Fig. 1). To prevent exposure of the tube internals to ambient air, this was done by moving an external magnet to force a magnet within the tube (Fig. 1), a procedure typically requiring about 1 s. After a known time, heating of the specimen was terminated and then the furnace opened to rapidly cool the quartz tube. Once the tube had reached ambient temperature, the ceramic boat was weighed to determine the total weight loss, and then kept in a sealed flask at 4 °C for later analysis.

Gases recovered from the gas sampling bag were analyzed by gas chromatography (GC) using a flame ionization detector (FID) and a thermal conductivity detector (TCD) to, respectively, quantify CH₄, C₂H₂, C₂H₄, C₂H₆ and H₂, CO, CO₂. The GC/FID analysis used an HP-5890 series chromatograph fitted with a GasPro™ polar capillary column (CSC 9609-02). The temperature program was 40 °C for 4 min, followed by a 15 °C/min ramp to 225 °C and then holding for 4 min. The injector (split–splitless) and detector temperatures were 265 and 285 °C, respectively. Nitrogen served as carrier gas (2 mL/min in the column), and the injected volume was 350 μ L. The GC/TCD analyses used a Perkin-Elmer Sigma I chromatograph fitted with two different columns each operated isothermally, also with a N₂ carrier gas. A 60/80-mesh molecular sieve 5A column (30 m long and 31 mm o.d.) at 50 °C for 15 min was used for H₂ and CO analysis. An 80/100 mesh Porapak R column (18 m long and 31 mm o.d.) at 5 °C for 10 min (using liquid nitrogen cooling) was used exclusively for CO₂ analysis. For both columns, the injector was kept at 150 °C and the detector at 175 °C while the auxiliary temperature was 136 °C. For all

gas chromatographic measurements conducted in the present work, the head column pressure was ≈ 69 kPa (10 psi). A standard mixture (Supelco) containing CH₄, C₂H₂, C₂H₄, C₂H₆, H₂, CO, and CO₂ in N₂ was used to calibrate the FID and TCD analyzers for quantitative determinations.

Material was recovered from the CF for chemical analysis by washing the outside surface of the CF with DCM. In some experiments, deposits of soot, i.e., fine particles of carbonaceous material, were observed on the CF. These deposits were washed into a receptacle with DCM and then subjected to ultrasonic extraction (two 10-min exposures at room temperature using a Sonifier®, Branson Ultrasonics Corp., at 350–450 W). The soot was then removed from the extract liquor by filtration. The DCM solutions were analyzed for PAH using gas chromatography coupled to mass spectrometry (GC–MS) and high performance liquid chromatography (HPLC). The GC–MS analyses used a Hewlett-Packard, HP-5890 series II chromatograph equipped with an HP-5 column connected to a mass spectrometer. The temperature program was 5 min at 35 °C followed by a 6 °C/min ramp to a temperature of 180 °C and there holding for 15 min. The injector and transfer line temperatures were heated to 180 and 170 °C, respectively. The column gas flow rate was 2 mL/min and the injection volume was 1 μ L. The HPLC analysis used a Hewlett-Packard HP-1090 M series II liquid chromatograph equipped with a Vydac 201TP54 polymeric C18 (length: 25 cm and inner diameter: 4.6 mm). The mobile phase program consisted of 60% H₂O:40% acetonitrile, linearly ramped to 100% acetonitrile in 40 min, followed by another 40 min ramp to 100% dichloromethane. The flow rate was 1.5 mL/min and the injection volume was 25 μ L. GC–MS and HPLC identified a wide variety of polycyclic aromatic hydrocarbons (PAH) in the DCM solutions [13]. Pyrene and cyclopenta[*cd*]pyrene concentrations were determined quantitatively, using HPLC with a UV–vis absorption diode array detector (DAD), calibrated with external standards, whereas relative concentrations were obtained for all other species.

Table 1
Effect of 500 and 650 °C heating on pyrene removal and cyclopenta[*cd*]pyrene (CPP) yields^a

	500 °C ^b			650 °C ^b		
	Neat soil	Neat pyrene	Soil + pyrene ^c	Neat soil	Neat pyrene	Soil + pyrene ^c
Initial sample						
Mass (mg)	161.8	12.3	143.5	179.8	9.9	154.3
Weight loss (%)	2.5	100	8.5	3.3	100	4.1
Pyrene recovery (%)						
Cold finger ^d	nd ^e	103 ± 8	93 ± 7	nd	109 ± 9	77 ± 6
Residue ^f	nd	nd	1	nd	nd	Traces ^g
CPP yield ^d	nd	nd	0.2 ± 0.1	nd	nd	0.7 ± 0.1

^a Gaseous products (for other temperatures, see Tables 2–4) were detected only from soil + pyrene at 650 °C. Yields in (wt% of sample) were: CH₄ 0.0176, C₂H₆ 0.015, C₂H₄ 0.028, and C₂H₂ 0.0026 (Total: 0.0632).

^b Vapor phase residence time (from sample boat to cold finger): 0.4 and 0.33 s at 500 and 650 °C, respectively.

^c Initial contamination level: 4.8 ± 0.1 wt% of soil.

^d Weight percent of initial pyrene charged and corrected for 50% collection efficiency of cold finger (see text).

^e Not detected.

^f In sample boat, wt% of initial pyrene charged.

^g Traces means less than approximately 5 µg present in total, i.e., ≈100 ng per 20 µL injection assuming an extracted volume of 1 mL.

3. Results

Tables 1–5 display the percentage of the initial charge of pyrene (PY₀) recovered from the cold finger (CF PY) and the residue in the sample boat, as well as the yields and identities of various by-products (light gases, PAH, and soot), from heating pyrene-contaminated soil (“soil + pyrene”) at furnace temperatures of 500, 650, 750, 1000, or 1100 °C. For selected conditions, also data on pyrene recoveries and by-products yields for heating the following controls are provided: neat (i.e., uncontaminated) soil, neat pyrene, neat

sand, contaminated sand (“sand + pyrene”), and, in Table 4, for “pretreated neat soil” (defined above). Information regarding experimental conditions and sources of uncertainty in these data is given in the footnotes of Tables 1–5. Note that with the exception of assays for pyrene in the sample residues, all the PAH yield data were corrected to account for material not collected on the cold finger. Such collection efficiency has been determined previously using the same experimental setup as in the present work [9]. In short, volatiles escaping the cold finger (blowby) were determined in two separate heating experiments of soil + pyrene

Table 2
Effects of 750 °C heating on pyrene removal and product yields^a

	Neat soil	Neat pyrene	Soil + pyrene ^b	Neat sand	Sand + pyrene ^b	Neat pyrene (<i>t</i> _{res} = 3.0 s) ^a
Sample mass (mg)	151.5	13.0	170.0	231.1	160.4	9.5
Weight loss (%)	9.1	100	13.1	1.5	3.2	100
Pyrene recovery						
Cold finger ^c	nd ^d	73 ± 6	60 ± 5	nd	43 ± 3	3.6 ± 0.2
Residue ^e	nd	nd	Traces ^f	nd	Traces	nd
CPP yield ^c	nd	0.2 ± 0.1	1.4 ± 0.1	nd	0.2 ± 0.1	nd
Gas yields ^g (wt% of sample)						
H ₂	nd	0.18	0.01	nd	nd	nd
CO	nd	nd	nd	nd	nd	0.59
CO ₂	0.4502	nd	0.44	nd	nd	9.24
CH ₄	0.0016	0.0224	0.037	0.0016	0.0112	0.016
C ₂ H ₆	0.003	nd	0.036	nd	0.009	nd
C ₂ H ₄	0.0056	0.028	0.0756	0.0028	0.129	0.0028
C ₂ H ₂	nd	nd	0.0104	0.0026	0.0026	0.0182
Total gas yields (%)	0.4502	0.2304	0.609	0.0070	0.1518	9.867

^a Vapor phase residence time (from sample boat to cold finger): 0.3 s, except for neat pyrene where a residence of 3.0 s was used.

^b Initial contamination levels: 4.8 ± 0.1 wt% of soil and 4.9 ± 0.1 wt% of sand.

^c Weight percent of initial pyrene charged and corrected for 50% collection efficiency of cold finger (see text).

^d Not detected.

^e In sample boat, wt% of initial pyrene charged.

^f Traces means less than approximately 5 µg present in total, i.e., ≈100 ng per 20 µL injection assuming an extract volume of 1 mL.

^g From sampling bag.

Table 3
Effects of 1000 °C heating on pyrene removal and product yields^a

	Neat soil	Neat pyrene	Soil + pyrene ^b	Sand + pyrene ^b
Sample mass (mg)	149.1	15.2	143.2	156.6
Weight loss (%)	20	100	23.7	6.8
Pyrene recovery				
Cold finger ^c	nd ^d	24 ± 2	13 ± 1	14 ± 1
Residue ^e	nd	nd	Traces ^f	nd
CPP yield ^c	nd	0.2 ± 0.1	1.2 ± 0.1	1.2 ± 0.1
Gas yields ^g (wt% of sample)				
H ₂	0.03	1.89	0.09	0.12
CO	nd	nd	0.364	nd
CO ₂	3.08	nd	7.48	0.88
CH ₄	0.0128	0.296	0.1104	0.0832
C ₂ H ₆	nd	nd	0.003	0.003
C ₂ H ₄	0.0084	0.0252	0.0308	0.0812
C ₂ H ₂	0.0104	0.039	0.0702	0.1014
Total gas yield (%)	3.1416	2.2502	8.1484	1.2688

^a Vapor phase residence time (from sample boat to cold finger): 0.24 s.

^b Initial contamination levels: 4.8 ± 0.1 wt% of soil and 4.9 ± 0.1 wt% of sand.

^c Weight percent of initial pyrene charged and corrected for 50% collection efficiency of cold finger (see text).

^d Not detected.

^e In sample boat, wt% of initial pyrene charged.

^f Traces means less than approximately 5 µg present in total, i.e., ≈100 ng per 20 µL injection assuming an extract volume of 1 mL.

^g From sampling bag.

at 1000 °C and neat pyrene at 650 °C. Almost identical PAH compositions of the cold finger and sampling bag catches, showing that there is not preferential loss of PAH from the cold finger, e.g., depending on molecular mass [9]. The weight of PAH in the sampling bag was about 70% that on the cold finger, implying a CF collection efficiency for

PAH of $[100/(100 + 70)] = 59\%$ [9]. In light of the collective uncertainties of the present PAH determinations, a collection efficiency of 50% has been assumed in the present work.

PAH yield data in Tables 1–5 are considered reliable within a factor of 2. However, due to the use of external standards for both species and taking into account the precision

Table 4
Effects of 1100 °C heating on pyrene removal and product yields^a

	Pretreated neat soil	Neat soil		Neat pyrene	Soil + pyrene	
		Run-1	Run-2		Run-1 ^b	Run-2 ^b
Sample mass (mg)	173.9	139.1	150.0	10.7	158.0	161.0
Weight loss (%)	20.9	18.8	21.3	100	22.9	23.7
Pyrene recovery						
Cold finger ^c	nd ^d	nd	nd	11 ± 1	12 ± 1	nd
Residue ^e	nd	nd	nd	nd	nd	nd
CPP yield ^c	nd	nd	nd	0.2 ± 0.1	1.4 ± 0.1	nd
Gas yields ^f (wt% of sample)						
H ₂	0.04	0.03	0.02	2.78	0.2	0.16
CO	0.308	0.588	nd	nd	0.308	0.784
CO ₂	8.36	9.24	7.48	nd	7.04	11.0
CH ₄	0.016	0.016	0.0144	0.4224	0.0928	0.080
C ₂ H ₆	nd	nd	nd	nd	nd	nd
C ₂ H ₄	0.0028	0.0028	0.0028	nd	0.0056	0.0028
C ₂ H ₂	0.0026	0.0182	0.0182	0.0858	0.0936	0.0702
Total gas yield (%)	8.7294	9.895	7.5354	3.2882	7.74	12.097

^a Vapor phase residence time (from sample boat to cold finger): 0.22 s.

^b Initial contamination levels: 4.8 ± 0.1 wt% of soil.

^c Weight percent of initial pyrene charged and corrected for 50% collection efficiency of cold finger (see text).

^d Not detected.

^e In sample boat, wt% of initial pyrene charged.

^f From sampling bag.

Table 5
Effects of furnace temperature and substrate on PAH yields and soot detection^a

PAH yield ^b (wt% of PY ₀)	650 °C			750 °C			1000 °C			1100 °C		
	Neat pyrene	Soil + pyrene ^c	Neat pyrene	Soil + pyrene ^c	Neat pyrene	Soil + pyrene ^c	Sand + pyrene ^c	Neat pyrene	Soil + pyrene ^c	Sand + pyrene ^c	Neat pyrene	Soil + pyrene ^c
Naphthalene	nd ^d	nd	nd	nd	nd	nd	nd	nd	nd	nd	0.1	0.1
Phenanthrene	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	0.02	0.1
Cyclopenta[<i>a</i>]/phenanthrene	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	0.03	0.1
Methylpyrenes	nd	16	nd	4	nd	nd	Traces ^e	nd	0.1	Traces ^e	nd	0.1
Dicyclopentapyrenes	nd	2	nd	5	nd	nd	Traces	nd	nd	Traces	nd	0.7
Benzo[<i>a</i>]pyrene	nd	Traces	nd	Traces	nd	nd	Traces	nd	0.1	Traces	nd	0.1
Benzo[<i>ghi</i>]-perylene	Traces	nd	1	Traces	Traces	Traces	Traces	0.2	0.1	0.1	0.1	0.2
Indeno[1,2,3- <i>cd</i>]pyrene	nd	nd	nd	1	nd	Traces	Traces	nd	0.1	0.2	0.03	0.1
Bipiryrenyls ^f	nd	nd	4	Traces	Traces	Traces	nd	3	0.7	1.4	3.0	0.6
Soot observed ^g	No	No	No	No	No	No	No	Yes	Yes	Yes	Yes	Yes

^a No PAH and soot were detected in 500 °C heating of neat pyrene or soil + pyrene.

^b Yields are semi-quantitative estimates, i.e., ± a factor of 2 (see text), for PAH recovered from the cold finger.

^c Initial contamination levels: 4.8 ± 0.1 wt% of soil and 4.9 ± 0.1 wt% of sand.

^d Not detected.

^e Traces means less than approximately 5 µg present in total, i.e., ≈100 ng per 20 µL injection assuming an extract volume of 1 mL.

^f Molecular structures for six of these C₃₂H₁₈ dimers of pyrene are given in Ref. [9].

^g Visually detected on the cold finger surface or reactor tube walls.

of the gravimetric determination of total masses, fractions of pyrene, and CPP in the DCM extracts are reliable to within ±10%.

The efficiency of soil decontamination can be estimated from the CF PY and residue PY data in Tables 1–5 for heating soil + PY. CF PY provides a lower bound on the *specific decontamination efficiency*, i.e., the percentage of the initial pyrene eliminated from the soil. This estimate is conservative because during heating, owing to chemical reactions within, on, or external to the soil, pyrene will be converted to products that report to the soil residue, the CF, or the reactor walls. If all pyrene in the heated soil residue is detected, 100% (residue PY) provides a check on the percentage of pyrene eliminated from the soil. Note however, that *total decontamination efficiency*, i.e., the percentage elimination from the soil of all exogenous matter, i.e., PY as well as PY-derived products, such as other PAH, will be less than the specific decontamination efficiency when products of PY conversion are retained in the treated soil.

4. Discussion

4.1. Neat pyrene

Table 1 shows that at 500 and 650 °C, neat pyrene is totally volatilized from the sample boat because the sample weight loss is 100% and recovery of the initial charge of pyrene (PY₀) from the CF is 100 ± 10%. These observations build confidence in the substantial reliability of the procedures used to collect, recover, and analyze vaporized pyrene. Aside from minuscule conversion to benzo[*ghi*]perylene at 650 °C (Table 5), there is no significant loss of PY by chemical reactions at these temperatures. At 750, 1000, 1100 °C, the weight loss for neat pyrene is also 100% (Tables 2–4), but with increasing temperature, the CF catch accounts for less and less of PY₀, while yields of light gases (Tables 2–4) and yields or diversity of PAH products increase (Table 5). Because no pyrene was detected in the residue samples, it is apparent that increasing amounts of this compound, i.e., up to ca. 27, 76, and 89%, respectively (Tables 2–4), are converted to other substances. Table 6 shows the percentage of PY₀ accounted for by CF PY, residue PY, cyclopenta[*cd*]pyrene, PAH other than CPP (obtained from Table 5), and light gases. The sum total of these five categories of products, also shown in Table 6, cannot account quantitatively for all of PY₀ at 750, 1000, and 1100 °C, but there are notable contributions from specific PAH. At 750 °C, bipiryrenyls and benzo[*ghi*]perylene (Table 5) account for 5% of PY₀. At 1000 and 1100 °C bipiryrenyls (Table 5) represent 3%, and H₂ (Tables 3 and 4) about 2 and 3%, respectively, and soot (Table 5) an unknown further amount. Small amounts (ca. 0.2 wt% of PY₀) of CPP were recovered from the cold finger in the 750, 1000, and 1100 °C experiments. CPP is a potent mutagen to bacterial and human cells in vitro [14,15]. Recognizing that the present data on PAH yields can be uncertain by up to a factor of two,

≥50% accountability for PY₀ is reasonable. The 500, 650, and 750 °C data readily meet this criterion whereas the 1000 and 1100 °C results fall short. Soot (Table 5) may account for much or all of the missing PY₀ at these two temperatures.

4.2. Neat soil

Weight loss from heating uncontaminated soil increases from 2.5 to about 20% (mean of two runs) as furnace temperature increases from 500 to 1100 °C (Tables 1–4). This soil matrix contains about 0.39 wt% organic carbon [12], so the formation of PAH upon heating cannot be ruled out a priori. However, no PAH were detected in any of the neat soil runs. Light gases were not detected at 500 and 650 °C (Table 1), and the yields of most light gases at 750, 1000, and 1100 °C were insignificant as a percentage of the observed soil weight loss (Tables 2–4). An exception is the yield of CO₂ at 1100 °C which amounted to 8.4 wt% of soil (mean of two runs) and equivalent to 1.9 mol/kg charge (Table 4). This would still account for less than half the 20% measured weight loss of soil at this temperature. Additional information about volatiles that may contribute to thermal weight loss of neat soil is available from previous work by Bucalá et al. [12]. These authors studied similar temperatures (350–1050 °C) as in the present work but employed much faster heating rates (1000 °C/s) as well as a considerably different apparatus, i.e., an electrical screen heater that rapidly diluted and quenched newly released volatiles. Thus, comparisons must be handled with care. In agreement with the present work, they found soil weight loss and CO₂ yields of about 21.4% and 10 wt% of soil, respectively, at 1030 °C. In contrast to the present observations, they found appreciable yields of CO at 1030 °C, i.e., ca. 30–40% (by mass) of the CO₂ yield, and non-negligible yields of CO at lower temperatures, e.g., 0.4 wt% of soil at 750 °C. At 1030 °C, Bucalá et al. [12] also found about 3–4 wt% of soil as “tars”, i.e., a less volatile liquid product that condensed on the walls of the soil heating chamber. They estimated that H₂O could account for another 1 wt% of soil and closed overall material balances within about 5%. In light of the work of Bucalá et al. [12], products not analyzed for in the present study, such as water and tars, could account for perhaps 1/4 of the soil weight loss at 1100 °C leaving roughly another 35% of the weight loss to be accounted for. The present findings of lower gas yields at lower temperatures, of low absolute yields of CO₂ and CO, and of much higher CO₂/CO ratios, may reflect differences in the two experimental techniques, or a possible under-recovery of CO in the present study.

4.3. Pyrene-contaminated soil

As evidenced from the absence of pyrene in the soil residues (save for 1% of PY₀ at 500 °C), heating at all temperatures resulted in specific decontamination efficiencies, i.e., elimination of PY₀ from the soil, of 99–100% (Table 6). However, the percentage of eliminated PY accounted for

by recovery on the cold finger (CF PY), i.e., 93 ± 7 , 77 ± 6 , 60 ± 5 , 13 ± 1 , and $12 \pm 1\%$, respectively, at 500, 600, 750, 1000, and 1100 °C (Table 6), clearly declined substantially with increasing temperature. Thus, with increasing temperature more and more pyrene is converted to other products, i.e., light gases, PAH, and substances not extracted by DCM, such as soot. At 650 °C, the different methylpyrene (MePY) and dicyclopentapyrene isomers (DiCPP), respectively, account for 16 and 2 wt% of the PY charged (Table 5) raising the imputed PY₀ accountability to a very respectable 96% (Table 6). At 750 °C, the yields of CPP (Table 2), MePY, DiCPP, and indeno[1,2,3-*cd*]pyrene (Table 5), respectively, are 1.4, 4, 5, and 1 wt% of PY₀, so that these four PAH plus CF PY (Table 2) account for over 71% of PY₀ (Table 6). As shown in Tables 2–4, the sum of all light gases was found to contribute between less than 1% at 750 °C and ≈10% at 1100 °C. The diversity of PAH products (Table 5) increases with increasing temperature with five and six different compounds detected in non-trace quantities at 1000 and 1100 °C, respectively. However, at 1000 and 1100 °C PY recoveries on the CF were only 13 and 12%, respectively (Tables 3 and 4). The gas plus PAH yields are too low to account for the remaining 87 and 88% of the PY₀. We believe that PY-derived soot (Table 5) is responsible for much of this under-recovery of PY₀. Yields of CPP increase with increasing temperature from 500 to 750 °C and then remain at around 1.2–1.4 wt% of PY₀ at 1000 and 1100 °C. With the remarkable exception of similar yields with sand + PY at 1000 °C, CPP yields from the various controls, i.e., neat PY, sand + PY, and neat soil [9] were either undetectable or substantially smaller than those from soil + PY at the same heating conditions. Benzo[*a*]pyrene (BaP) was detected in trace amounts when heating PY-contaminated soil at 650 and 750 °C and in yields of 0.1 wt% of PY₀ at 1000 and 1100 °C (Table 5). Further, BaP was not a product of heating PY alone at any of these four temperatures or of heating sand + PY controls at 750 and 1000 °C (the two temperatures studied for pyrene-contaminated sand, Table 5). These observations show that heating soil contaminated with a non-bioactive PAH generates at least two by-product PAH that are bioactive, i.e., BaP and CPP that are known to mutate bacterial cells [14] and human cells [15] in vitro. BaP is also a human carcinogen [16]. Plausible enabling roles for soil itself in these and other features of soil thermal decontamination are discussed below.

4.4. Pyrene-contaminated sand

Control experiments with pyrene-contaminated sand, prepared by means of the same procedure as the contaminated soil (see above), have been conducted at 750 and 1000 °C. Many soils are rich in sand, for instance the present matrix contains about 31 wt% of it [12]. The comparison of thermal treatment of pyrene-contaminated soil with control runs using neat pyrene (described above) and pyrene-contaminated sand allows for the assessment of the role of heterogeneous effects and of possible contributions of light gases present in the soil

Table 6
Material balances for pyrene and weight loss of pyrene-contaminated soil or sand^a

Weight percent of initial pyrene (PY) in indicated product									Weight loss of PY-contaminated soil or sand		
Sample	Furnace temperature (°C)	CF PY	Residue PY ^b	CF CPP	Other CF PAH	Light gases	Total	Soot observed	WL _c predicted (%) ^c	WL _o observed (%)	Initial pyrene ^d (%)
Pyrene	500	103 ± 8	nd ^e	nd	nd	nd	nd	No	na ^f	na	na
Soil + PY	500	93 ± 7	1	0.2 ± 0.1	nd	nd	94.2 ± 7	No	7.18	8.5	-27.5
Pyrene	650	109 ± 9	nd	nd	Traces ^g	nd	109 ± 9	No	na	na	na
Soil + PY	650	77 ± 6	Traces	0.7 ± 0.1	18	0.06	95.8 ± 6	No	7.94	4.1	+80.0
Pyrene	750	73 ± 6	nd	0.2 ± 0.1	5	0.23	78.4 ± 6	No	na	na	na
Soil + PY	750	60 ± 5	Traces	1.4 ± 0.1	10	0.61	72.0 ± 5	No	13.46	13.1	+7.5
Sand + PY	750	43 ± 3	Traces	0.2 ± 0.1	Traces	0.15	43.4 ± 3	No	6.33	3.2	+63.9
Pyrene	1000	24 ± 2	nd	0.2 ± 0.1	3.2	2.3	29.7 ± 2	Yes	na	na	na
Soil + PY	1000	13 ± 1	Traces	1.2 ± 0.1	1.1	8.15	23.4 ± 1	Yes	23.84	23.7	+2.92
Sand + PY	1000	14 ± 1	nd	1.2 ± 0.1	1.7	1.27	18.2 ± 1	Yes	≥6.33	6.8	≥-9.59
Pyrene	1100	11 ± 1	nd	0.2 ± 0.1	3.3	3.29	17.8 ± 1	Yes	na	na	na
Soil + PY: I	1100	12 ± 1	nd	1.4 ± 0.1	2.1	7.74	23.2 ± 1	Yes	22.70	22.9	-4.17
Soil + PY: II	1100	nd	nd	nd	nd	12.1	12.1	Yes	22.70	23.7	-20.83

^a Data from Tables 1–5. See text and footnotes of Tables 1–5 for details on furnace operation, sample acquisition and chemical analysis.

^b Residue in sample boat after experiments.

^c This value is obtained by adding the weight losses separately measured for soil or sand and neat pyrene at the same temperature, weighted by the mass fraction of soil or sand and pyrene in the pyrene-contaminated soil/sand. In the case of sand, a weight loss for neat material was only measured at 750 °C and amounted to 1.5 wt%. This value was corrected to a basis of sand + 4.9 wt% pyrene and the resulting 1.43 wt% used for all temperatures.

^d Predicted–experimental percent weight loss relative to initial pyrene contamination, i.e., 4.8 wt% in the case of soil and 4.9% in the case of sand.

^e Not detected.

^f Not available.

^g Traces means less than approximately 5 µg present in total, i.e., ≈100 ng per 20 µL injection assuming an extract volume of 1 mL.

matrix [12] in the formation of toxic by-products, such as cyclopenta[*cd*]pyrene and benzo[*a*]pyrene. The absence of PY in the sand residues (other than traces of PY at 750 °C) shows that heating at 750 and 1000 °C (Tables 2 and 3) eliminates essentially all of the pyrene from this substrate. Pyrene recovered from the cold finger (CF PY), respectively, accounted for 43 ± 3 and $14 \pm 1\%$ of PY₀ at these two temperatures (Table 6). Further, in light of their environmental importance, observed yields of other PAH must be considered significant, e.g., cyclopenta[*cd*]pyrene was 0.2 and 1.2 wt% of PY₀ at 750 and 1000 °C, respectively (Table 6), and at 1000 °C benzo[*ghi*]perylene, indeno[1,2,3]pyrene, and bipyrenyls yields of 0.1, 0.2, and 1.4 wt% of PY₀ were found, respectively (Table 5). This leaves 57% of the PY₀ still unaccounted for at 750 °C, respectively (100—column 8, Table 6). Plausible sources of this missing PY₀ are deduced by comparing the observed and predicted weight loss for PY-contaminated sand. The latter is obtained by adding the weight losses separately measured for sand and for neat PY at the same temperature, weighted by the mass fraction of sand and PY in the PY-contaminated sand. A weight loss for neat sand was only measured at 750 °C and amounted to 1.5%. Correcting this value to a basis of sand + PY (i.e., 1.43 wt%) and adding in the contribution of the 4.9% PY contamination, results in a predicted weight loss of 6.33%. The 3.2% weight loss for sand + PY actually observed at 750 °C is 3.13% less, corresponding to 63.9% (3.13/4.9) of PY₀. This 64% shortfall is in remarkably close agreement with the 57% of PY₀ unaccounted for by volatile products and the DCM extract of the substrate. These findings suggest that at 750 °C in the presence of sand there is substantial conversion of the PY to non-volatile product(s) that are not extractable from the residue with DCM. Such products may include high MW organic compounds or solid carbon-rich matter, e.g., soot or similar carbonaceous material. The observed weight loss for sand + PY (6.8%) at 1000 °C exceeds that predicted by the above procedure ($\geq 6.33\%$) (Table 6). This suggests that few if any pyrene reaction products are retained in the sand or ceramic boat. This inference is based on the chemically reasonable assumption that sand weight loss may increase slightly from 750 to 1000 °C (hence the “greater than or equals” sign), but not significantly. However, at 1000 °C volatile products and residue DCM extract accounted for only 18% of the PY₀ (column 8, Table 6) even though all pyrene was eliminated from the sand (Table 3). Thus, about 82% of the initial charge of PY must be accounted for by a product that is neither retained in the soil residue nor quantified as light gases or CF PAH. We conclude that soot particles account for this “missing” PY at 1000 °C. This soot is believed to be generated primarily in the high temperature region between the boat and the CF (Region II, Fig. 1).

4.5. Effects of method of soil contamination

The pyrene solvent (DCM) could conceivably modify the soil by dissolving native organic components, swelling

clays, etc. Therefore, an experiment was performed to assess whether the soil contamination procedure affected soil behavior during thermal treatment. A specimen of the EPA synthetic soil matrix was treated according to our standard procedure for installing a known weight of PY in the soil, except the PY was omitted. The resulting soil specimen, “pretreated neat soil” in Table 4, was then heated at a furnace temperature of 1100 °C using our standard procedures. Aside from a seven-fold smaller acetylene yield, the weight loss and yields of light gaseous products are similar to those for heating neat soil at this furnace temperature (Table 4).

4.6. Effects of increased volatiles residence time

To assess effects of vapor phase reactions of PY or its reaction products, in the region between the sample holder and the CF, a sample of neat pyrene was heated at a furnace temperature of 750 °C using 1/10 the helium carrier gas flow rate normally used at this temperature. In addition to the gas phase residence time, carrier gas flow rate affects the dilution of PY vapor adjacent to the sample holder, and thus the concentration of PY vapor at the exit of the sample holder and the rate of PY mass transfer from the sample holder. The sample holder presents a blunt body obstacle to the carrier gas flow. Changes in the carrier gas flow rate may therefore also modify the importance of flow recirculation in the vicinity of the boat, which could in turn affect PY evaporation and mixing with the carrier stream. Nevertheless, for present purposes, it is assumed that the main effect of the 10-fold decrease in carrier gas flow rate was a factor of 10 increase in the residence time of PY vapor in Region II, i.e., between the sample boat and collection on the cold finger (Fig. 1). Compared to the normal vapor phase residence time of 0.3 s, the ca. 3 s case does not change the PY weight loss (100%) or the amount of PY detected in the sample boat residue (none). However, there was a dramatic decrease in the amount of PY recovered from the CF, namely from 73 ± 6 wt% of PY₀ at 0.3 s to only 3.6 ± 0.2 wt% PY₀ at 3 s. Moreover, the significant yield of the mutagen CPP (0.2 ± 0.1 wt% PY₀) at 0.3 s declined to zero at 3 s. These observations support the conclusion that appreciable secondary reactions of PAH vapors occur in Region II at 750 °C in the case of increasing residence times, resulting in destruction of pyrene and of at least one PY-derived PAH, i.e., CPP. It is not easy to exegete the differences in the gaseous product yields at these two residence times (Table 2) because the most prominent differences are in the yields of oxygen-containing gases, i.e., CO and CO₂ which were not detected with neat PY at 0.3 s at 750 °C (or at any of the other four temperatures), but were observed in yields of 0.59 and 9.24 wt% PY₀ for the 3.0 s 750 °C PY experiment. Contamination by ambient air (unlikely given the experimental procedure) and subsequent oxidation could explain at least partially this discrepancy. Unfortunately, detailed analyses for other PAH (Table 5) were not performed for the 3 s residence time PY experiment.

4.7. Soil–pyrene interaction effects during decontamination

Several pieces of evidence suggest that chemical, and possibly, physical interactions between the soil and pyrene impact decontamination efficiency as well as yields and identities of resulting by-products. Table 6 (columns 10–12) compares the observed weight loss (WL_o) of PY-contaminated soil with a predicted weight loss (WL_c), calculated assuming no effect of soil on PY removal and no effect of PY on soil weight loss. WL_c is obtained by adding the weight losses separately measured for soil/sand and neat pyrene, weighted by their mass fractions in the contaminated soil or sand. At temperatures of 750, 1000, and 1100 °C, WL_o and WL_c are in good agreement. However, at 650 °C, WL_c is substantially higher than WL_o whereas most of the initially charged pyrene (PY_0) (96%) is readily accounted for by pyrene and other PAH, particularly methylpyrenes, collected at the cold finger (Tables 1 and 5). Thus, we conclude that the shortfall in WL_o at 650 °C is caused by errors in the gravimetric determination of this quantity, at least partially due to relative small absolute values (Table 1). At 500 °C, WL_o exceeds WL_c by an amount equivalent to 27% of PY_0 even though 93% of PY_0 was collected on the CF and only 1% was recovered from the soil residue. A plausible explanation is that at this temperature PY augments the weight loss of soil but also experimental uncertainties similar to those at 650 °C cannot be excluded. Increase of weight loss in the presence of pyrene has been reported by Saito et al. [8] but for a very different apparatus. These authors measured weight loss, products yields, and products compositions from heating neat or contaminated (4.75 wt% PY) samples of this same soil matrix at 1000 °C/s to temperatures from 400 to 1000 °C, under 20 kPa of helium using an electrical screen heater reactor that allowed for rapid dilution and quenching of newly released volatiles. They found that at about 530 °C WL_o began to exceed WL_c and that the “excess” WL became greater with increasing temperature up to about 700 °C. They proposed augmentation of soil volatilization by pyrene or pyrene reaction products above a certain temperature as an explanation for this behavior.

4.7.1. Catalysis of pyrene conversion

In the present experiments, the apparent (imputed) pyrene conversion can be estimated as 100%—the PY recovered, i.e., from the CF and the residue in the sample boat. Table 6 displays the results for heating neat PY, PY + soil, and PY + sand at various temperatures. The presence of soil enhances PY conversion at every temperature except 1100 °C. The effect is strong at 500 and 650 °C, considerable at 750 °C, and modest but clear at 1000 °C. These observations suggest a catalytic effect of one or more soil minerals (including silica, see below) in augmenting PY conversion at lower temperatures. At the highest temperature (1100 °C) the kinetics of PY pyrolysis are already sufficiently rapid to make catalysis redundant. Table 6 further shows that the enhancement of PY

conversion is even greater with sand at 750 °C and that there is no significant difference between soil + PY and sand + PY at 1000 °C. This suggests that silica in the soil may be especially active for PY conversion at lower temperatures, i.e., 500–750 °C. The effects of soil and sand on specific products are considered next.

The fraction of PY_0 accounted for by “other” PAH, (Table 6, column 6: other CF PAH) is similar for neat PY and PY + soil, i.e., within a factor of 3 or better, except at 650 °C, where yields of other PAH are insignificant for heating neat PY but 18 wt% of PY_0 for contaminated soil, again suggesting soil–PY interactions during heating, because no PAH have been detected from heating neat soil at temperatures from 250 to 1000 °C [9]. Further, for several experiments there are considerable differences in the yields of individual PAH when heating neat pyrene in comparison to soil + pyrene. For example, at all five temperatures the yields of CPP from soil + PY exceed those from neat PY by a factor of 5 or more (Table 6). Other notable differences in PAH yields (in wt% of PY_0) for heating PY + soil versus neat PY are (Table 5): at 650 °C: methylpyrenes (16 versus nd) and dicyclopentapyrene (2 versus nd); at 750 °C: methylpyrenes (4 versus nd), dicyclopentapyrenes (5 versus nd), benzo[ghi]perylene (traces versus 1), indeno[1,2,3-*cd*]pyrene (1 versus nd), and bipyrenyls (traces versus 4); at 1000 °C: methylpyrenes (0.1 versus nd), benzo[*a*]pyrene (0.1 versus nd), indeno[1,2,3-*cd*]pyrene (0.1 versus nd), and bipyrenyls (0.7 versus 3); 1100 °C: phenanthrene (0.1 versus 0.02), methylpyrenes (0.1 versus nd), dicyclopentapyrenes (0.7 versus nd), benzo[*a*]pyrene (0.1 versus nd), and bipyrenyls (0.6 versus 3). All of these differences in PAH yields are large enough to suggest the existence of different chemical pathways when heating neat PY versus PY + soil. Interactions between the PY or its decomposition products and the soil or products of soil decomposition, during heating are plausible causes for these differences.

To further assess the hypothesis of a catalytic effect, note that similar PY elimination efficiencies, PY recoveries on the CF, CPP yields, and other PAH product spectra, were recorded for heating PY-contaminated soil and PY-contaminated sand at 1000 °C (Tables 5 and 6). However, at 750 °C differences with possible mechanistic implications are discernible. To wit, in comparison to soil + PY, the sand + PY experiment resulted in substantially lower yields of CPP, H₂, methane, and acetylene (Table 2) and of methylpyrenes, dicyclopentapyrenes, and indeno[1,2,3-*cd*]pyrene (Table 5), as well as in no detectable benzo[*a*]pyrene or bipyrenyls (Table 5). Further, the sand + PY PAH product composition measured at 750 °C was more similar to that obtained for neat PY than for soil + pyrene. Other than benzo[ghi]perylene, indeno[1,2,3-*cd*]pyrene and bipyrenyls (traces, traces and nd for sand + PY versus 1, nd and 4 wt% for neat pyrene), no PAH were detected in both cases (Table 5). Because the soil itself contains substantial silica (31 wt%), agreement between soil + PY and sand + PY results and differences

with data from the heat treatment of pure PY, is consistent with a catalytic effect of silica. On the other side, agreement between sand+PY and neat PY results suggests some other effect unique to soil, e.g., catalysis by a non-silica mineral or participation of products of soil decomposition, not available in sufficient concentrations from sand, PY, or sand+PY. For instance, at 750 °C, C₂H₂ was not detected in the gaseous products resulting from heating PY, but was four-fold more abundant from heating soil+PY than from sand+PY (Table 2). Thus, acetylene addition to PY or its reaction products may contribute appreciably to the production of CPP at 500, 650, and 750 °C when heating soil+PY, whereas silica-catalyzed cracking may reduce the yields of PY-derived benzo[ghi]perylene, bipyrenyls, and benzo[a]pyrene when heating soil+PY at 650, 750, and 1000 °C, and sand+PY at 750 and 1000 °C (Table 5). The higher yields of methane from soil+PY versus neat PY at 650 and 750 °C suggest that reactions of methyl radicals with PY may be responsible for the much higher yields of methylpyrenes from soil+PY in comparison to the heat treatment of pure PY at 650 and 750 °C (Table 5).

4.8. Assessment of chemical pathways for pyrene conversion

The present data allow further testing of hypotheses of Richter et al. [9] and equilibrium predictions of Pope et al. [17] on how pyrene is transformed to other PAH during soil thermal treatment. Richter et al. [9] proposed equimolar reaction of PY with acetylene derived from soil or pyrene as a plausible CPP formation pathway when heating PY-contaminated soil. However, these authors lacked data on acetylene yields to test this hypothesis and one motivation for the present study was to provide such data by measuring acetylene yields from thermal treatment of soil under conditions similar to those of Richter et al. [9]. In the present

work, at all five temperatures the combined molar yields of acetylene from neat PY and neat soil fall far short of the corresponding molar yields of CPP from soil+PY (Table 7). Thus, if soil and PY were heated in isolation, they would produce insufficient acetylene to account for all the CPP observed from heating pyrene-contaminated soil, even if their C₂H₂ yields were combined. However, the molar C₂H₂ yield from heating soil+PY at 650, 750, 1000, and 1100 °C (no C₂H₂ was detected at 500 °C) and from heating sand+PY at 750 and 1000 °C (the only two temperatures with sand+PY data) is in all cases much larger than the combined molar yield of C₂H₂ from neat PY and neat soil at the corresponding temperature (Table 7). These observations imply that soil catalyzes production of substantial additional acetylene from PY, and that silica, which amounts to 31 wt% of the present soil, may be primarily responsible. Table 7 also shows that the molar acetylene yields from soil+PY and sand+PY are far less than the corresponding molar yields of CPP at the same heating temperature. This is not cause to reject CPP formation via equimolar reaction of acetylene with pyrene (or the corresponding 1- and 4-pyrenyl radicals) [9] because in all the present runs, the measured acetylene yield represents only C₂H₂ that exited the heating apparatus and thus survived reactions with PY (or other substances). It is possible that much more acetylene was produced than detected when PY underwent pyrolysis in the presence of soil or sand and reacted subsequently with PY to produce the observed CPP. Thus, Richter et al.'s proposed mechanism [9] remains open, awaiting more definitive testing, e.g., through use of PY labeled with ¹³C to track sources of carbon in the C₂H₂ and CPP products.

One possible source of acetylene is scission of PY into equimolar quantities of phenanthrene (PH) and C₂H₂. Thus, if PH is subsequently stable it serves as a proxy for acetylene derived from PY by this mechanism. Richter et al. [9] found excellent correspondence between molar yields of PH and

Table 7

Yields of acetylene, phenanthrene (PH) and cyclopenta[cd]pyrene (CPP) from pyrene-contaminated soil and sand^a

Furnace temperature (°C) ^b	Neat pyrene (PY)			Neat soil		Soil + pyrene			Neat soil + neat PY ^c	Sand + PY
	PH	C ₂ H ₂	CPP	C ₂ H ₂	CPP	PH	C ₂ H ₂	CPP	C ₂ H ₂	C ₂ H ₂
500	nd ^d	nd	nd	nd	nd	nd	nd	0.179	na	na
650	nd	nd	nd	nd	nd	nd	0.0042	0.626	na	na
750	nd	nd	0.179	nd	nd	nd	0.017	1.25	na	0.0041
1000	nd	0.003	0.179	0.017	nd	nd	0.114	1.07	0.020	0.161
1100(1) ^e	0.023	0.007	0.179	0.029	nd	0.114	0.152	1.25	0.036	na
1100(2) ^e	na ^f	na	na	0.029	nd	na	0.114	nd	>0.028	na
750(3s) ^b	na	0.0014	nd	na	na	na	na	na	>0.0014	na

^a Yields for pyrene-contaminated soil and sand are normalized to a basis of moles per mole of initial pyrene contamination. Data for neat soil refer to 4.8 wt% of pyrene present in contaminated soil. For instance, an acetylene yield of 0.0039 wt% in neat soil at 1000 °C (Table 3) corresponds to 0.004 mol of C₂H₂ per kg charge. 4.8 wt%, i.e., 48 g of pyrene are equal to 48/202 = 0.2376 mol. Therefore, 0.004/0.2376 = 0.0168 (0.017) represents the number of moles acetylene collected from neat soil normalized to the basis of the amount of pyrene present in pyrene-contaminated soil.

^b Except for the indicated experiment at 750 °C the vapor phase residence time of pyrene between the sample boat and the cold finger is 0.2–0.4 s.

^c The sum of the independently determined contributions of neat pyrene and of soil to the amount of collected acetylene, both normalized to the amount of pyrene present in pyrene-contaminated soil (see footnote a).

^d Not detected.

^e Two experiments were performed at 1100 °C.

^f Data not available.

CPP when heating neat PY at 1000 °C, but CPP/PH molar ratios of order 15–20 when heating sand + PY or soil + PY at the same temperature. In the present study, PH was not detected at temperatures below 1100 °C (Table 5), and at this temperature the CPP/PH molar ratios were about 8–10 for heating neat PY and PY + soil, respectively (Table 7). Thus, in the presence of soil or sand, acetylene production from PY occurs without equimolar production of PH or the rates of PH destruction exceed those of its formation at temperatures below 1100 °C.

Pope et al. [17] computed thermodynamic driving forces for transformations of various PAH by isomerization and acetylene addition under conditions relevant to soil thermal treatment, using molecular mechanics methods to estimate key thermodynamic properties of the PAH. The present results are consistent with their prediction that at temperatures from 500 to 1100 °C CPP production by acetylene addition to PY is strongly favored thermodynamically.

A semi-quantitative kinetic analysis is presented in Supplementary data. Kinetic parameters for the following global pathways for pyrene conversion have been determined: (1) vapor phase pyrolysis, (2) catalysis by sand, and (3) catalysis by or reaction with, soil or its decomposition products.

Overall, it has been found that in the investigated temperature range the main reason for enhanced pyrene conversion in the presence of soil or sand beds consists in increased residence times. Light gas species released due to the thermal treatment, such as acetylene and methane, lead the formation of other, pyrene-derived PAH, e.g., methylpyrenes, cyclopenta[*cd*]pyrene, and benzo[*a*]pyrene.

5. Relevance to industrial practice

The present experiments exposed small batch samples of pyrene-polluted soil as well as various controls, to relatively well-controlled heating conditions at temperatures relevant to practical-scale soil thermal cleaning processes. Note however that these experiments did not expose soil, contaminants, or their reaction products to exogenous oxygen or steam. Thus, the present study was neither designed nor intended to forecast the efficiency of soil or by-product cleanup potentially attainable in practical-scale soil remediation technologies in which thermal treatment is supplemented by high temperature oxidation, steam gasification, hydrogenation, and/or other cleaning measures (e.g., adsorption on activated carbon). Nevertheless, the present results are relevant to current and candidate larger scale thermal processes for soil decontamination. Studies in the absence of exogenous oxygen, at any scale, provide a benchmark against which O₂-induced effects can be disentangled. Similar arguments apply to other reactive gases, such as steam and H₂. Further, O₂-free experiments help diagnose and interpret off-specification performance of oxidative (and other reactive) systems when stoichiometrically required oxygen (or other reactant) potentials are

vitiated, e.g., owing to mixing imperfections, temperature excursions, under-feeding of oxidant, or overfeeding of soil. They also help illuminate the behavior of non-oxidative technologies, for example, heating in thermal plasmas, baths of molten material, and other pyrolytic appliances. The present observations of PAH by-products including at 500, 650, 750, 1000, and 1100 °C cyclopenta[*cd*]pyrene, a known mutagen to bacterial and human cells, *in vitro*, and at 1000 and 1100 °C benzo[*a*]pyrene, a known human carcinogen, show that bioactive by-products can be formed during thermal treatment of soil contaminated with a non-mutagen, i.e., pyrene. Therefore, soil thermal cleaning operations should be designed to completely destroy or decontaminate the initial contaminant as well as hazardous by-products of the heating process. Plausible means to this end include appending or interdicting soil pyrolysis by oxidation, e.g., in the main heating chamber and/or in downstream after-treatment chambers and/or by adsorption of unwanted by-products on active carbon (for subsequent further decontamination). Also important are means for on-line detection of PAH and other unwanted by-products in the treatment reactor and in process effluent streams, e.g., using laser-induced fluorescence (LIF) [18,19]. In soil thermal decontamination as in all technologies the efficaciousness of these and other means of performance implementation and assessment must be evaluated at the largest scale of planned operation.

6. Conclusions

The present work shows that essentially all of an exogenous PAH contaminant, i.e., pyrene, can be removed from soil or sand, by heating for a few tens of seconds to a temperature as low as 500 °C for soil or 750 °C for sand. No exogenous steam or oxidant (e.g., air) is needed. However, this work also demonstrates that complete elimination from soil of an initially targeted organic contaminant, does not necessarily avoid the need to deal with toxic by-products. Thus, at all five temperatures studied, PAH other than pyrene were detected among the by-products of heating pyrene-contaminated soil, including significant quantities of the potent bacterial cell and human cell mutagen, cyclopenta[*cd*]pyrene at 500, 650, 750, 1000, and 1100 °C, and of the human carcinogen benzo[*a*]pyrene at 1000 and 1100 °C. Pyrene conversions and yields of acetylene, CPP, and other PAH for pyrene-polluted soil are higher than the sum of data from of separate heat treatment of pyrene and soil, implying that soil–pyrene interactions significantly impact soil decontamination chemistry. Among the putative causes are heterogeneous catalysis by silica and possibly other minerals in the soil, and reactions of pyrene or its decomposition products with light gases, such as acetylene, produced by thermal decomposition of organic matter in the soil, and in more substantial quantities by soil (probably silica) catalyzed decomposition of pyrene itself. Good pyrene material balances were observed at lower temperatures (i.e., ≤650 °C) whereas at higher temperatures

($\geq 1000^\circ\text{C}$), quantitative assays for soot (which were not performed here) are needed to account for all products of PY conversion. Contributions of vapor phase pyrolysis and reaction within the soil bed to pyrene conversion were assessed by means of a kinetic analysis provided in [Appendix A](#). Increase of residence time was found to be the main reason for the enhanced conversion of pyrene in the case of the presence of a soil or sand matrix. Arrhenius expressions describing pyrene conversion in the vapor phase as well as in a soil bed have been deduced. Other, pyrene-derived PAH, e.g., methylpyrenes, cyclopenta[*cd*]pyrene, and benzo[*a*]pyrene, were formed by reaction with light gas species, such as acetylene and methane, released during the thermal treatment of soil.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the on-line version, at [doi:10.1016/j.jhazmat.2005.06.019](https://doi.org/10.1016/j.jhazmat.2005.06.019).

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