# Chemical Characterization and Bioactivity of Polycyclic Aromatic Hydrocarbons from Non-Oxidative Thermal Treatment of Pyrene-Contaminated Soil at 250–1,000°C

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In this paper we report yields, identities, and mutagenicities of products from heating a polycyclic aromatic hydrocarbon (PAH)-contaminated, Superfund-related synthetic soil matrix without exogenous oxygen. We heated batch samples of soil pretreated with 5.08 wt% (by weight) pyrene in a tubular furnace under a constant flow of helium gas at 250, 500, 750, and 1,000 ± 20°C. Dichloromethane (DCM) extracts of cooled residues of heated soil and of volatiles condensed on a cold finger after 1 sec residence time at furnace temperature were assayed gravimetrically and analyzed for PAH by HPLC, HPLC coupled to mass spectrometry, and gas chromatography coupled to mass spectrometry. All four temperatures volatilized pyrene and generated other PAHs, including alkylated pyrenes. We detected bioactive PAHs in the product volatiles: cyclopenta[*cd*]pyrene (CPP) at 750 and 1,000°C and benzo[*a*]pyrene (BaP) at 1,000°C. We found a clean soil residue, i.e., no pyrene or other DCM extracts, only at 750°C. Control experiments with uncontaminated soil, pyrene, and Ottawa sand plus 4.89 wt% pyrene revealed no CPP or BaP production from soil itself, but these experiments imply that pyrene interactions with soil, e.g., soil-bound silica, stimulate CPP and BaP production. We detected mutagenicity to human diploid lymphoblasts (*in vitro*) in volatiles from 1,000°C heating of soil plus pyrene and sand plus pyrene, and in the residue from 500°C heating of soil plus pyrene. Three plausible pathways for pyrene conversion to other PAHs are *a*) a reaction with light gas species, e.g., soil- or pyrene-derived acetylene; *b*) loss of $C_2$-units followed by reaction with a PAH; and *c*) dimerization with further molecular weight growth via cyclodehydrogenation. This study shows that thermal treatment of PAH-polluted soil may generate toxic by-products that require further cleanup by oxidation or other measures. *Key words*: benzo[*a*]pyrene, cyclopenta[*cd*]pyrene, decontamination, mutagenicity, PAHs, polycyclic aromatic hydrocarbons, pyrene, soil, thermal. *Environ Health Perspect* 108:709–717 (2000). [Online 23 June 2000]
*http://ehpnet1.niehs.nih.gov/docs/2000/108p709-717richter/abstract.html*

Contaminated soil harms the environment when natural or human forces transfer its pollutants to other venues, e.g., surface or subsurface aquifers and the ambient atmosphere. Efficient cleanup of contaminated soils without hazardous by-products is thus a major goal of environmental remediation initiatives such as the U.S. Superfund Basic Research Program (*1*). Thermal decontamination technologies are of significant scientific and practical interest because they can provide high destruction and removal efficiencies for organic pollutants (*2*), and they have often been selected for cleanup of Superfund sites (*2,3*). Further, new methods for above-ground and *in situ* treatment may innovate and extend the applicability of soil thermal cleaning technologies. Broadly based public acceptance is essential to siting and operating environmental technology in the United States. For soil thermal remediation, a notable concern is that process residues or effluents may jeopardize human health (*4*), for example, because of inadequate cleaning of targeted pollutants or generation of hazardous by-products (*5*) during routine or off-specification operations. Detailed scientific and engineering understanding of soil thermal treatment is useful in the design, operation, monitoring, and innovation of remediation technologies and should thus be of interest to diverse stakeholders.

Laboratory scale research has mimicked thermal and chemical environments of practical processes to elucidate underlying details of soil thermal decontamination, for example, see Saito et al. (*6*). One technique ohmically heated (~1,000°C/sec) captive samples of powdered soil supported on a thin metal foil (*7–9*). Bucalá et al. (*7*) determined total weight loss as well as the yields and global release rates of carbon monoxide, carbon dioxide, methane, acetylene, ethylene, and ethane, and tars from pyrolysis of a U.S. Environmental Protection Agency (EPA) synthetic soil matrix at 350–1,050°C. Exogenous contaminants were not added to the soil. Saito and colleagues (*8,9*) studied the effects of temperature (400–1,000°C) and heating rate on elimination of pyrene contamination from this EPA synthetic soil. Pyrene removal (imputed gravimetrically) rose significantly with increasing temperature to near 100% at approximately 530°C. Above 530°C, the total weight loss of contaminated soil exceeded the sum of the corresponding weight loss from neat soil plus the initial weight of pyrene contamination (*8,9*). Saito and colleagues (*8,9*) inferred that chemical reactions of soil with pyrene or pyrene decomposition products augmented soil volatilization.

Gilot et al. (*10*) used a thermogravimetric analyzer (TGA; Cahn System 113, Cahn Instruments, Madison, WI) to study pyrene removal (inferred from weight loss data) during much slower heating (5–50°C/min) of shallow beds of clay particles contaminated with approximately 8 wt% (by weight) pyrene. They found that rates of pyrene release from the soil bed were approximately 5-fold lower than those from heating pure pyrene under similar conditions. A mathematical model described pyrene release in terms of evaporation from a liquid shell surrounding each soil particle, followed by diffusive transport through the voids in the soil bed and then through a concentration boundary layer between the top of the soil pile and the top of the TGA crucible (*10*). This model reasonably correlated removal of approximately 70% of the pyrene. Pichon et al. (*11*) used similar TGA and modeling methods to determine the evaporation behavior of naphthalene, hexachlorobenzene, and 4-chlorobiphenyl, under conditions of interest in soil thermal decontamination. Using a TGA, a heating rate of 5°C/min, and temperatures up to 450°C, Risoul et al. determined rates and

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We thank R.M. Frederick of the U.S. Environmental Protection Agency and S. Rosenthal from Foster Wheeler Enviresponse Inc. for providing soil samples and information on the properties and composition of this soil. We also acknowledge helpful discussions with P. Gilot and C. Pope.

Financial support was provided by National Institute of Environmental Health Sciences grant P42 ESO4675-12 (MIT-Superfund Hazardous Substances Basic Research Program).

Received 7 December 1999; accepted 30 March 2000.

extents of thermal removal of these compounds from reference soils of different composition under 1 atm of $N_2$ (*12*), and under 0.1 and 1.0 atm of air (*13*).

Tognotti et al. (*14*) and Flytzani-Stephanopoulos et al. (*15*) used an electrodynamic balance to study adsorption and desorption of toluene and carbon tetrachloride between a gas stream and single particles of clay or carbon. Rates and extents of pollutant uptake depended upon the type of particle, with accessible internal surface impacting the amount absorbed. Mukherjee et al. (*16*) detected different bipyrenes, condensed products of bipyrene dehydrogenation; cyclopenta[*cd*]pyrene (CPP), a mutagenic polycyclic aromatic hydrocarbon (PAH) (*17*); and soot, from pyrolysis of pyrene between 927 and 1,227°C. Pope et al. (*18*) used molecular mechanics methods to calculate thermodynamic driving forces for molecular weight (MW) growth or intramolecular rearrangement of PAHs during simulated soil thermal treatment between 300 and 1,100°C. They found that CPP formation by adding $C_2H_2$ to pyrene became increasingly thermodynamically competitive with increasing temperature.

Despite previous valuable contributions, there is a need to better define and understand soil thermal treatment conditions that eliminate targeted PAH contaminants without generating hazardous products. In this paper we report on effects of temperature and soil itself on pollutant removal, and on yields, identities, and mutagenicities of products from thermal treatment of a pyrene-contaminated (~ 5 wt%) Superfund-related soil matrix under helium at 250–1,000°C. No single soil-PAH combination can represent all PAH-polluted soils. We used a synthetic soil matrix prepared for the EPA (*19*) to reflect attributes of soils at U.S. Superfund sites. This soil has been found to be free of anthropogenic pollutants (*20,21*), and it has been used in other decontamination studies (*7–9,21,22*). Pyrene has been found in complex organic mixtures at hazardous waste sites. It has a molecular weight, volatility (boiling point 393°C), and thermal chemical reactivity pertinent to a midboiling range PAH. In our experiments we did not heat soil in the presence of exogenous oxygen, but the results are relevant to commercial practice. Another thermal technology, stripping with steam—with and without vacuum—at temperatures up to approximately 150°C, is of interest for *in situ* cleaning of organics from polluted soils, for example, volatile and semivolatile dense nonaqueous phase liquids such as perchloroethylene (*23–25*). The present study is not directly related to steam thermal stripping because we have focused on higher temperatures (250–1,000°C) and have not investigated effects of exogenous steam.

## Materials and Methods

We studied pyrene-contaminated soil to determine contributions of soil or pyrene to PAH formation or modification (*6*), pyrene, uncontaminated soil, and pyrene-contaminated sand. Analysis by HPLC revealed two trace contaminants in the untreated pyrene: 4H-cyclopenta[*def*]phenanthrene and an unknown compound with a pyrene-like ultraviolet-visible (UV-vis) spectrum and that eluted just before pyrene. We presume that this unknown compound is similar to pyrene, but a definitive chemical structure could not be deduced even from HPLC coupled to mass spectrometry (HPLC-MS) and gas chromatography coupled to mass spectrometry (GC-MS). Bucalá et al. (*7*) provide information on the elemental, mineral, and soil constituents of the EPA synthetic soil matrix. In the present study, we used a 63–125 µm size fraction of this soil prepared in our laboratory by mechanical dry sieving. This size range reduces intraparticle temperature and concentration gradients during heating. Soil was contaminated with 5.08 ± 0.10 wt% pyrene using a procedure described by Saito and colleagues (*8,9*). We dried the sized soil particles for 2 days over Drierite (anhydrous calcium sulfate; W.A. Hammond, Xenia, OH) in a desiccator. We then covered an unbroken layer of soil with a concentrated solution of pyrene (99%, Aldrich, Milwaukee, WI) in dichloromethane (DCM) and sealed it in an inverted cylindrical weighing jar for 12 hr to provide time for the soil to adsorb pyrene from the solvent. The solvent was then allowed to evaporate slowly over 8–10 hr in a specially treated, inverted wide-mouth jar (*8*). The resulting residue, that is, the contaminated soil, was then redried in the desiccator before use.

Approximately 31 wt% of the EPA soil is sand. To probe for effects of silica, we contaminated samples of Ottawa Sand (EM Science, Gibbstown, NJ) with 4.89 (± 0.10) wt% of pyrene using the same procedure as for soil (*8,9*). The sand particle size fraction, 53–180 µm, prepared by mechanical dry-sieving was skewed toward sizes > 120 µm. We tested a sample of untreated sand for organic contamination by extracting with DCM. We detected no extractables by weighing the residue after DCM evaporation or by GC-MS analysis of the extract. The residue from evaporation of pure solvent was zero to within the 1 µg detection limit of the microbalance.

We placed batch specimens of known initial weight (typically 15–21 mg, determined gravimetrically) in a 5-cm-long porcelain combustion boat. We preheated a cylindrical 30 cm long, 1.65 cm i.d. quartz tube (the reaction tube) to 250, 500, 750, or 1,000°C ± 20°C in a horizontally configured cylindrical furnace. To collect condensible products, we then inserted a cold finger (CF), a water cooled, sealed cylindrical tube, into the quartz tube from its downstream end. To begin a soil heating experiment, we inserted the combustion boat and specimen into the quartz tube from its upstream end to a depth of 5 cm (i.e., from the furnace entrance to the middle of the boat). To eliminate air, we purged the tube with helium at a pressure slightly above ambient (i.e., slightly > 1 atm) during insertion of the boat and throughout heating of the specimen. The furnace tube, reaction tube, and cold finger are essentially coaxial, with the CF tip about 15 cm downstream from the middle of the boat. The average residence time of volatiles between the soil and the CF tip was approximately 1 sec. A type K thermocouple was located between the outside wall of the reaction tube and the inside wall of the furnace approximately 10 cm downstream of the middle of the combustion boat. We maintained samples at furnace temperature for 45–60 sec. The experiment was then ended by removing the boat. The helium purge was immediately ceased, and the furnace was opened to expedite cool down of the quartz tube.

We recovered PAHs for chemical analysis by ultrasonic extraction of the sample boat residue and the CF deposit with DCM. Wash solutions were sonicated using a Model 450 Sonfier (Branson Ultrasonics Corp., Danbury, CT) at 350–450 W for about 20 min without exogenous heating or cooling. Sonication was used to enhance dissolution and recovery for analysis of products soluble in DCM and partitioned onto the soil or onto fine carbonaceous particulates (soot) recovered from the CF, the boat, or the quartz tube walls. After a heating experiment, we obtained two wash solutions for sonication. The residue in the combustion boat as well as the boat itself were washed carefully with DCM. The resulting wash liquid had a volume of approximately 15–20 mL and typically contained soil or sand particulates entrained during the washing procedure. The wash liquid and particulates were placed in the sonicator chamber. We prepared a second wash solution by using DCM to wash the CF and, for runs at 1,000°C, the inside walls of the reaction tube in the vicincity of the CF. This wash liquid sometimes contained fine particulates, especially at higher temperatures (~ 1,000°C), which we presumed to be soot formed by pyrolysis of some pyrene. After approximately 20 min of sonication, each specimen of wash liquid was filtered. We measured extract yields (the mass of the residue left after evaporation of the filtered DCM) gravimetrically for each of the two specimens using a procedure specially developed by Lafleur et

al. (*26*) to minimize losses of volatile PAHs from environmental samples.

We analyzed portions of the resulting solutions for PAHs using HPLC with a UV-vis absorption diode array detector (HPLC/DAD). Procedures are described in detail elsewhere (*27*). In brief, we used a Hewlett Packard 1090 M Series II liquid chromatograph (Hewlett Packard, Rockwell, MD) equipped with a Vydac 201TP54 polymeric C18 column (25 cm in length with a 4.6 mm i.d. (Separations Group, Hesperia, CA). The mobile phase program consisted of 60% $H_2O$: 40% acetonitrile linearly ramped to 100% acetonitrile in 40 min, followed by another 40 min ramp to 100% DCM. The flow rate was 1.5 mL/min, and we injected 25 µL using an autoinjector for each analysis after solvent exchange to DMSO. Standards were not available for some important PAH products, for example, bipyrenyls, their condensation products, and pyrene derivatives (alkylated pyrenes). Consequently, to obtain semiquantitative estimates of the relative abundances (by mass) of these and other PAHs, the DAD signal was integrated from 235 to 500 nm using the new Hewlett Packard enhanced integration algorithm. This approach is, of course, an approximation. To assess its reliability, we determined mass response factors, that is, the mass of a PAH injected per area of its HPLC/DAD chromatogram peak, using four PAHs for which standards were available, (phenanthrene, fluoranthene, pyrene, and benzo[*a*]pyrene). We analyzed standard solutions in the present study covering the range of concentrations of these four PAHs by the HPCL/DAD method. The resulting four response factors showed deviations of approximately ± 10%. Pyrene derivatives, bipyrenyls, and bipyrenyl condensation products exhibit similar UV-vis spectra to pyrene. Thus, when calibration standards are lacking, the DAD integration method is a reasonable approach for semiquantitative determinations of the relative mass abundances of PAHs, especially PAHs with similar UV-vis spectra.

To assist in product identification, in particular that of bipyrenyls and their condensation products, we analyzed selected extracts by HPLC/DAD coupled to mass spectrometry (Sciex, Thornhill, Ontario) using an atmospheric pressure chemical ionization interface and an analytical protocol similar to that described above. The identity of some species with lower molecular masses (e.g., pyrene derivatives) was determined by gas chromatography (Hewlett-Packard Model 5890 Series II Plus) coupled to a mass selective detector (Hewlett-Packard Model 5972) using a cross-linked phenyl-methyl-siloxane stationary phase (Hewlett-Packard HP-5MS column, 0.25 mm i.d. × 30 m). The column temperature program consisted of a 1.5 min hold at 50°C, followed by a linear ramp to 310°C at 8°C/min, and a final hold at 310°C for 10 min. The injector temperature was 250°C. No solvent exchange was performed for GC analysis, that is, the samples were kept in DCM.

## Results

***CF collection efficiency and pyrene material balances.*** Figure 1 shows the chemical structures of several PAHs identified in the present study. Table 1 summarizes furnace temperatures, initial sample masses, and masses of the DCM extracts of the soil residues and the CF for each experiment. Table 1 also presents standard deviations for several DCM extract masses calculated from three or more determinations using aliquots of the extract solution. Table 2 lists PAHs identified in the

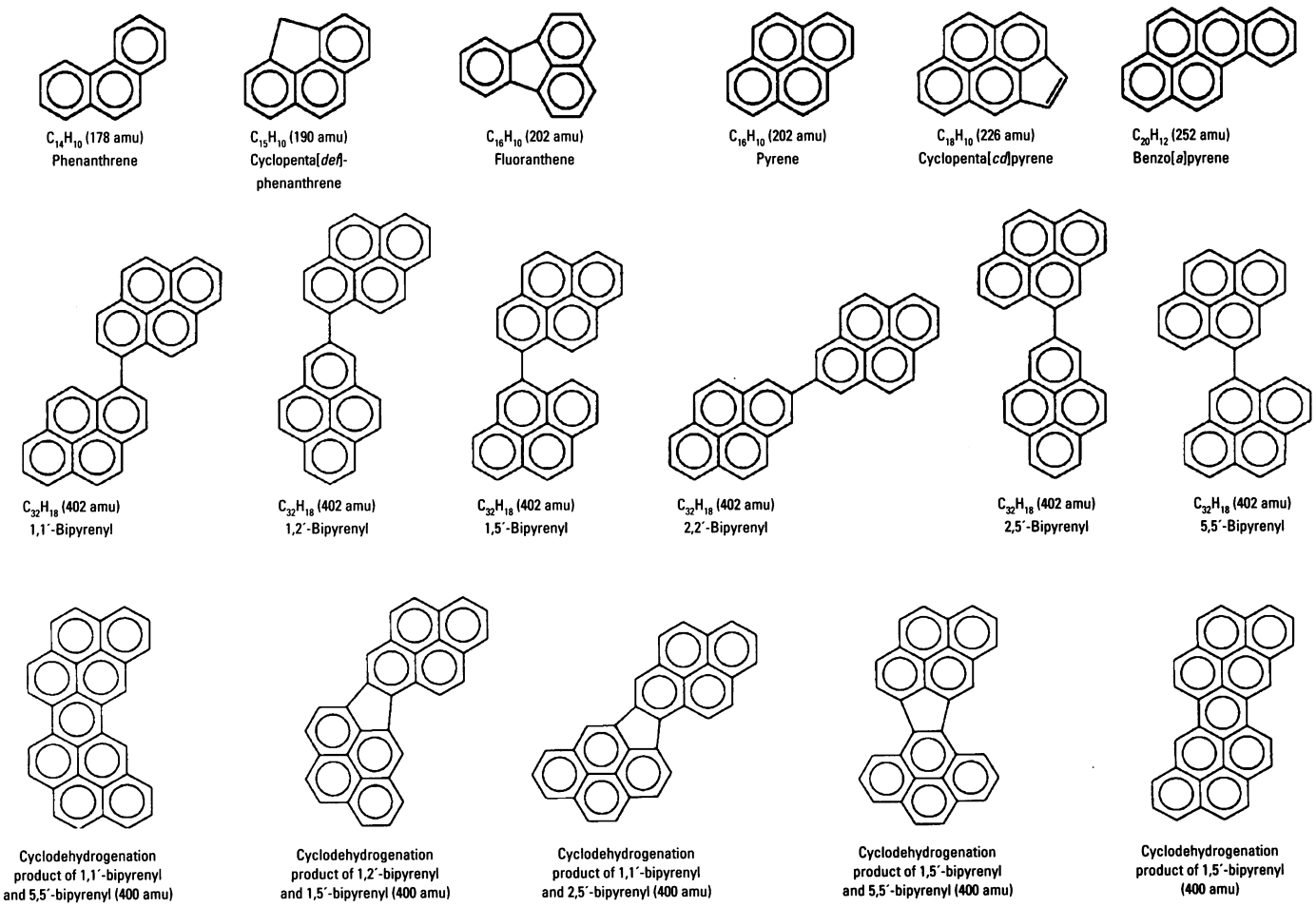


**Figure 1.** Chemical structures of PAHs.

soil residue and CF extracts, and a semiquantitative measure of their relative mass abundance, (the percent contribution of the mass of each compound or compound class to the total UV-vis absorption signal of the extract). The repeatability of the chromatographic analyses is estimated at ± 1%.

The collection efficiency of the CF was separately assessed by heating soil and pyrene at 1,000°C and neat pyrene at 650°C, and by collecting the CF effluent (blowby) in gas sampling bags (Supelco, Bellefonte, PA). In both tests, HPLC analysis of the sampling bag catch and the CF DCM extract gave nearly identical compositions, showing that CF blowby does not affect PAH relative abundances. The weight of material recovered from the sampling bag was 70% of that extracted from the CF, implying a CF collection efficiency of 59% [(100)/(100 + 70)]. Considering these measurements plus the ± 10% deviations in the mass calibrations of the UV-vis detector broadband integration technique and the possibility that some organic by-products may be UV-vis transparent, we estimate that the PAH relative abundances (Table 2) are uncertain to no worse than ± 35%. Data on yields of PAH and DCM extracts (Tables 1–6) are estimated to be uncertain by no more than a factor of 2.

Table 3 presents the yields of pyrene and DCM extractables recovered from the CF and the combustion boat (i.e., the residue) after heating. The data are presented as the percentage of the initial weight of pyrene used in each experiment. Thus, a pyrene material balance can be estimated from Table 3. In 7 of the 12 runs (2, 3, 9, 10, 13–15), the unaccounted for pyrene ranges from –22 to + 34%; thus, the pyrene balance closes within the factor of 2 uncertainty stated above. Two more runs (12 and 16) also meet this criterion when the 59% CF collection efficiency is taken into account, that is, the actual CF pyrene yields could be as high as 75 and 53%, respectively (1.70 × 44 and 1.70 × 31).

Runs 1, 4, and 11 exhibit pyrene shortfalls (77, 79, and 84%, respectively) that are too high to be explained in terms of CF collection efficiencies alone. We hypothesize, but at this stage cannot prove, that pyrene condensation on the reactor tube walls upstream of the CF accounts for much of the pyrene shortfall in run 1 (heating of pyrene at 250°C). This temperature (250°C) is well below the boiling point (bp) of pyrene at atmospheric pressure (393°C). For condensation to occur, the ambient vapor pressure of pyrene must exceed that allowed by vapor–liquid equilibrium at 250°C. For 250°C heating of pyrene plus sand (run 13), the CF catch of pyrene was much better, 66% versus < 23% for run 1. This provides a clue as to what may be happening in run 1. We hypothesize that the 0.79 mg pyrene precontacted with the sand bed (Table 1, run 13) evaporated more slowly than the 15.6 mg pyrene (Table 1) in run 1. This is consistent with earlier experiments in our laboratory (*10*) in which pure pyrene heated in a TGA was found to evaporate 5 times more rapidly than pyrene premixed with powdered clay. In the present experiments, a higher pyrene evaporation rate in run 1 would create higher local partial pressures of pyrene in the reactor tube and enhanced opportunity for pyrene loss by condensation upstream of the CF. In our runs at higher temperatures (≥ 500°C), there is no driving force for pyrene condensation at 1 atm pressure because pyrene is above its bp (393°C).

Pyrene and its reaction products are the only plausible source of CF DCM extractables in the neat pyrene and sand plus pyrene experiments. Because pyrene decomposition accelerates with increasing temperature, the

**Table 1.** Experimental conditions including the temperature, masses of the initial sample, pyrene, and the DCM extractables in the residue and in the material collected on the CF.

| Sample | T (°C)[a] | Initial sample Total (mg) | Initial sample Pyrene (mg) | DCM residue (mg) | Collected on CF (mg) |
|---|---|---|---|---|---|
| 1 (pure pyrene) | 250 | 15.6 | 15.6 | 0.00 | 3.96 ± 0.02 |
| 2 (pure pyrene) | 500 | 16.6 | 16.6 | 0.00 | 12.46 + 0.41 |
| 3 (pure pyrene) | 750 | 16.1 | 16.1 | 0.00 | 15.43 ± 0.40 |
| 4 (pure pyrene) | 1,000 | 16.8 | 16.8 | 0.00 | 5.67 ± 1.18 |
| 5 (uncontaminated soil) | 250 | 15.6 | 0.00 | 0.21 ± 0.09 | 0.00 |
| 6 (uncontaminated soil) | 500 | 17.5 | 0.00 | 0.00 | 0.00 |
| 7 (uncontaminated soil) | 750 | 18.7 | 0.00 | 0.08 ± 0.01 | 0.00 |
| 8 (uncontaminated soil) | 1,000 | 17.6 | 0.00 | 0.00 | 0.00 |
| 9 (soil + pyrene) | 250 | 18.9 | 0.96 | 0.93 ± 0.07 | 0.37 ± 0.0 |
| 10 (soil + pyrene) | 500 | 20.2 | 1.03 | 0.36 ± 0.04 | 0.83 ± 0.07 |
| 11 (soil + pyrene) | 750 | 20.4 | 1.04 | 0.00 | 0.24 ± 0.03 |
| 12 (soil + pyrene) | 1,000 | 20.7 | 1.05 | 1.12 ± 0.02 | 0.67 ± 0.08 |
| 13 (sand + pyrene) | 250 | 16.1 | 0.79 | 0.09 ± 0.02 | 0.54 ± 0.03 |
| 14 (sand + pyrene) | 500 | 18.7 | 0.91 | 0.00 | 1.18 ± 0.07 |
| 15 (sand + pyrene) | 750 | 19.3 | 0.94 | 0.00 | 1.08 ± 0.02 |
| 16 (sand + pyrene) | 1,000 | 20.0 | 0.98 | 0.00 | 0.44 ± 0.03 |

[a]± 20°C.

**Table 2.** Major species detected in the DCM extracts of the residue and in the material collected on the CF.

| Sample | T (°C)[a] | Major PAHs in residue | Major PAHs collected on the CF |
|---|---|---|---|
| 1 **Pure pyrene** | 250 | No residue observed | Pyrene (> 91.8%) |
| 2 **Pure pyrene** | 500 | No residue observed | Pyrene (> 98.6%) |
| 3 **Pure pyrene** | 750 | No residue observed | Pyrene (83%), FA (0.31%); (≈ 5%) |
| 4 **Pure pyrene** | 1,000 | No residue observed | PH (0.95%), pyrene (67.25%), **CPP** (0.89%), bipyrenyls (≈ 15%), condensation products of different bipyrenyls (≈ 15%) |
| 5 Uncontaminated soil | 250 | No PAHs detected | NA |
| 6 Uncontaminated soil | 500 | No PAHs detected | NA |
| 7 Uncontaminated soil | 750 | No PAHs detected | NA |
| 8 Uncontaminated soil | 1,000 | No PAHs detected | NA |
| 9 **Soil + pyrene** | 250 | Pyrene (63%), pyrene derivatives (> 30%) | Pyrene (94%), pyrene derivatives (3.3%) |
| 10 **Soil + pyrene** | 500 | Pyrene (28%), pyrene derivatives | Pyrene (71%), pyrene derivatives (> 25%) |
| 11 **Soil + pyrene** | 750 | No PAHs detected | Pyrene (68%), **CPP** (2.33%)[b], pyrene derivatives (> 25%) |
| 12 **Soil + pyrene** | 1,000 | No PAHs detected | PH (0.4%), pyrene (69%), pyrene derivatives (≈ 10%), **CPP** (8.7%)[b], **BaP** (0.46%), bipyrenyls (5.7%) |
| 13 Sand + pyrene | 250 | Pyrene derivatives, no pyrene | Pyrene (> 96%) |
| 14 Sand + pyrene | 500 | No PAHs detected | Pyrene (> 94%) |
| 15 Sand + pyrene | 750 | No PAHs detected | Pyrene, (76.4%), pyrene derivatives (2.4%), bipyrenyls (13%) |
| 16 Sand + pyrene | 1,000 | No PAHs detected | PH (0.7%), pyrene (68.7%), **CPP** (11.2%)[b], **BaP** (1.4%), bipyrenyls (12.8%) |

Abbreviations: BaP, benzo[*a*]pyrene; FA, fluoranthene; NA, not applicable; PH, phrenanthrene. Potentially mutagenic species are indicated in bold.
[a]± 20°C. [b]Coeluting with a pyrene derivative.

nonpyrene portion of these extracts should therefore be greater at higher temperatures. The data in Table 3 support this expectation, that is, they compare the nonpyrene extract yields at 250 and 500°C versus those at 750 and 1,000°C for heating neat pyrene (runs 1 and 2 vs. runs 3 and 4) and for heating sand plus pyrene (runs 13 and 14 vs. runs 15 and 16). Thus the imputed pyrene accountability in run 4 (1,000°C) could increase to 34% (21% pyrene + 13% pyrene-derived extractables). After further correcting for the CF collection efficiency (34 × 1.70 = 58%), the imputed pyrene material balance falls within a factor of 2. Further, at 1,000°C soot was visually observed on the CF and in the furnace chamber, but its yield was not quantified. Here "soot" is operationally defined as solid carbonaceous particulate matter insoluble in DCM. In light of Tesner and Shurupov's observation of 56–59.5% soot yields from 1,100–1,350°C pyrolysis of pyrene (*28*), we suspect that an appreciable fraction of the 79% pyrene shortfall at 1,000°C reflects pyrene conversion to soot.

For run 11, heating soil plus pyrene at 750°C, the pyrene material balance (Table 3) is more difficult to rationalize. If pyrene is the only source of DCM extracts, the pyrene material balance in run 11 would increase to 22 × 1.70 = 37% (also crediting for the CF recovery factor). This clearly falls short of our factor of 2 criterion. However, we cannot rule out soil as a possible source of DCM extracts at higher temperatures (500–1,000°C). No PAHs (Table 2) were observed in heating uncontaminated soil at any of the four temperatures, but in the residue from heating neat soil, we did observe extractables that amounted to 0.43 wt% of the soil (Table 1). Further, other studies in our laboratory (*8,9*) found evidence that at > 530°C pyrene augments volatilization of this same soil type over that observed with neat soil. Thus, we are left with the hypothesis that some of the pyrene in run 11 is lost by conversion to material not recovered by DCM extraction.

***Pyrene pyrolysis.*** Table 3 shows no pyrene or extractables in the residue, implying that pyrene was completely removed from the heating boat, presumably by evaporation, at all four temperatures. However, the presence of by-product PAHs in the CF extracts from 750 and 1,000°C (Table 2), including the mutagens fluoranthene (at 750°C) and CPP (at 1,000°C), shows that a clean residue does not necessarily imply nontoxic volatiles. Recoveries of the initial pyrene as CF condensate varied from roughly 20 to 80% (Table 3). The pyrene material balance at 500 and 750°C is quite reasonable in light of the uncertainties of the present techniques.

The CF extract at 750°C (Table 2) contained fluoranthene (FA), MW 202 (0.31%), and at least five of the six possible bipyrenyl isomers (Figure 1) of MW 402 (5%). FA formation by isomerization of pyrene (MW 202) is unlikely in light of the high activation energy needed to form a 5-membered ring from a 6-membered ring, and in light of Scott and Roelofs' (*29*) report of FA equilibrium with two other 5-membered ring PAHs, acephenanthrylene and acenanthrylene, but not pyrene, in experimental studies of FA pyrolysis at 920, 1,000, and 1,115°C.

The CF extract at 1,000°C (Table 2) contained five isomers (15%) identified by HPLC-MS as bipyrenyls (Figure 1) and at least four other isomers (15%) with MW 400 and significantly higher elution times than bipyrenyls, taken as bipyrenyl condensation products. Mukherjee et al. (*16*) detected the latter class of compounds from pyrene pyrolysis and attributed their formation to dimerization and cyclodehydrogenation of different bipyrenyls. Thus we believe the soot detected here at 1,000°C was formed primarily by direct polymerization of aromatic moeities rather than by sequential addition of $C_2H_2$ (*16*). Phenanthrene (PH; 0.95%) and CPP (0.89%) were also detected in the 1,000°C CF extract. There is too much PH to be attributed only to degradation of the 4-H-cyclopenta[*def*]phenanthrene impurity in the pyrene. Decomposition of pyrene itself must therefore contribute to the production of this compound. The mutagen CPP (*17*) could be produced by pyrene reaction with $C_2$-moities formed by pyrene decomposition. $C_2$ moities refer to two-carbon species such as $C_2H_2$ and to free radicals such as $C_2H$ radical or $C_2H_2$ diradicals ($C_2$).

***Uncontaminated soil.*** Pyrolysis of uncontaminated soil gave no CF extractables but yielded soil residue extracts equivalent to 1.01 and 0.43 wt% of the soil at 250 and 750°C (Table 1). One possible source of this material is thermal decomposition of soil organic matter, e.g., humic substances (*30–32*). Bucalá et al. (*7*) found comparable or greater yields (0.5–1.5 wt% of soil) of a possibly related product from pyrolysis of this same soil (1,000°C/sec to 350–1,050°C), that is, a tar-like substance volatilized from the soil and condensed on various surfaces and filters in the heating apparatus. Thus, despite the small organic carbon assay of this soil, 0.39% (*7*), pyrolysis can still generate leveraged yields of condensables. No PAHs were detected in any of the soil or CF extracts (Table 2) or in the DCM extract of unheated, uncontaminated soil.

***Pyrene-contaminated sand.*** Unheated, uncontaminated Ottawa sand gave no DCM extracts. For sand plus pyrene, we recovered DCM extracts from the CF for all four treatment temperatures, but we recovered DCM extracts from the residue only at 250°C (Table 1). As discussed above, the pyrene

**Table 3.** Semiquantitative estimates of pyrene and DCM extractable yields from heating pyrene-contaminated soil or controls.[a]

| | | | wt% of initial pyrene | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| | | | Pyrene yields | | | DCM extractables | | | |
| Material | Run | Final Temp (°C)[b] | Residue[c] | CF[d,e] | Unaccounted for[f] | Residue[c] | CF excluding pyrene[d,e] | CF including pyrene[d,e] | Total[g] |
| Pyrene | 1 | 250 | 0 | < 23 | 77 | 0 | < 2 | < 25 | < 25 |
| | 2 | 500 | 0 | > 74 | 26 | 0 | < 1 | < 75 | < 75 |
| | 3 | 750 | 0 | 80 | 20 | 0 | 16 | 96 | 96 |
| | 4 | 1,000 | 0 | 21 | 79 | 0 | 13 | 34 | 34 |
| Sand + pyrene | 13 | 250 | 0 | 66 | 34 | 11 | < 3 | < 69 | < 80 |
| | 14 | 500 | 0 | 122 | –22 | 0 | < 8 | < 130 | < 130 |
| | 15 | 750 | 0 | 88 | 12 | 0 | 27 | 115 | 115 |
| | 16 | 1,000 | 0 | 31 | 69 | 0 | 14 | 45 | 45 |
| Soil + pyrene | 9 | 250 | 61 | 36 | 3 | 97 | 2 | 38 | 135 |
| | 10 | 500 | 10 | 57 | 33 | 35 | 23 | 80 | 115 |
| | 11 | 750 | 0 | 16 | 84 | 0 | 6 | 22 | 22 |
| | 12 | 1,000 | 0 | 44 | 56 | 107 | 20 | 64 | 171 |

Temp, temperature.
[a]No PAH extracts were detected from heating neat (uncontaminated) soil or sand. [b]± 20°C. [c]Recovered by methylene chloride (DCM) extraction of combustion boat residue. [d]Collected on a water-cooled CF and recovered by DCM extraction. [e]The measured collection efficiency of the CF trap was 59% (see "Results"); thus, values in this column may be low by as much as a factor of 1.70. [f]This quantity equals 100% minus the yields of pyrene measured by extracting the residue and CF; it includes pyrene not collected, pyrene converted to soot (see "Results"), and pyrene converted to other compounds, some of which may contribute to the DCM extracts (see "Results"). [g]Sum of DCM extracts of residue and CF.

recoveries fall within a factor of 2, directly at 250, 500, and 750°C, and after correcting for the CF collection efficiency at 1,000°C (Table 3). Soot was visually observed at 1,000°C but its yield was not quantified. Aside from minor quantities of pyrene derivatives at 250°C, we detected no PAHs in the residue extracts at any of the four temperatures (Table 2). Several different PAHs were found in the CF extracts at 750 and 1,000°C (Table 2), but pyrene derivatives (in minor quantities) were detected only at 750°C. Plausible sources of pyrene derivatives are discussed below. Five or six bipyrenyl isomers (Figure 1)were detected and together contributed significantly (13%) to the CF extracts at 750 and 1,000°C (Table 2). Their absolute yields were approximately 60% lower at 1,000°C as compared to 750°C, owing to the correspondingly lower CF extract yields at this temperature (Figure 2). The CPP and phenanthrene yields at 1,000°C are discussed below.

***Pyrene-contaminated soil.*** The pyrene material balances at all four temperatures are discussed above, including factors (CF blow-by, pyrene conversion to other products) that could account for the appreciable pyrene shortfalls (Table 3) at 750 and 1,000°C. The quantity (Tables 1 and 3) and composition (Table 2) of DCM extracts in the soil residue after heating provides a measure of soil cleaning. Only the 750°C residue showed neither PAH nor other DCM extracts. The 250 and 500°C residues revealed DCM extracts, including pyrene derivatives. The 1,000°C residue showed no PAHs but did contain non-PAH extractables equivalent to 107 wt% of the original pyrene (1.12/1.05, run 12; Tables 1 and 3). Pyrene and other PAHs were detected in the CF extracts at all four temperatures. The compositional diversity of these PAHs increased with temperature from 500 to 1,000°C (Table 2). Thus the soil was cleaned of pyrene without recontamination with PAH or other DCM extracts only at 750°C. However, all four temperatures polluted the vapor stream with pyrene and other PAHs (Tables 1 and 2).

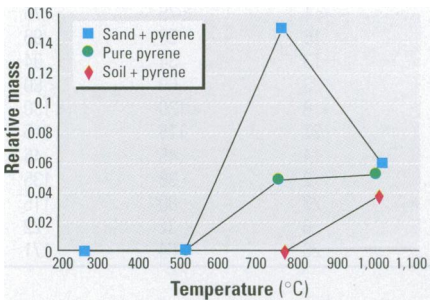


**Figure 2.** Mass of bipyrenyls recovered from the CF as a fraction of the initial mass of pyrene as affected by treatment temperature.

Other than pyrene, a class of PAHs designated pyrene derivatives were the only PAHs detected in the soil residue and CF extracts at 250 and 500°C (Table 2). These compounds also accounted for significant fractions of the CF extracts at 750 and 1,000°C (Table 2). Some of these compounds were identified by GC-MS as pyrene molecules substituted with alkyl groups such as methyl, ethenyl, or ethynyl. At 1,000°C, phenanthrene contributed modestly (~ 0.4–1%) to the CF extracts from pyrene plus soil (and from neat pyrene and pyrene plus sand). After accounting for the difference in extract yields, there is no significant difference in the phenanthrene yields as a percentage of initial pyrene (Table 6). Five or more bipyrenyl isomers contributed a total of 5.7 wt% to the 1,000°C CF extract from pyrene plus soil (Table 2). For heating at 750°C, bipyrenyl yields differed strongly for soil plus pyrene, pyrene, and sand plus pyrene (Figure 2). Further, bipyrenyl yields exhibited different effects of increasing pyrolysis temperature from 750 to 1,000°C, that is, an increase, essentially no change, and a strong decrease, respectively (Figure 2).

***Bioactive PAH.*** Benzo[*a*]pyrene (BaP) and/or CPP were detected in CF extracts from pyrene, sand plus pyrene, and soil plus pyrene at 750 and/or 1,000°C (Tables 2, 4, 5). BaP and CPP are mutagenic to bacterial cells (*33*) and human cells (*17*) *in vitro*. There are different scientific opinions regarding the relevance of mutagenicity in single cell model systems to genetic or other morbidity in humans. Nevertheless, it is prudent to identify thermal treatment conditions that give rise to by-products that exhibit this form of bioactivity. Further, a molecular biologic pathway linking BaP to human lung cancer has been established (*34*). Tables 4 and 5, respectively, present CPP and BaP yields, normalized to initial pyrene mass, as affected by pyrolysis temperature and starting material. CPP was obtained from heating pyrene, soil plus pyrene, or sand plus pyrene at 1,000°C, and from soil plus pyrene at 750°C. This suggests that soil opens up a lower temperature pathway for pyrene conversion to CPP, unattainable with pure pyrene or pyrene plus sand. At 1,000°C, BaP was not detected from heating pure pyrene (Tables 2 and 5), but within the factor of 2 uncertainty of the current experimental methods, heating of soil plus pyrene and sand plus pyrene at 1,000°C gave similar BaP yields (Table 5). These findings suggest that silica stimulates pyrene conversion to BaP at this temperature. Another bacterial cell mutagen, FA, was detected in the 750°C CF extract from pyrolysis of pyrene (Table 2). Given the detection limits of our HPLC, the small (~ 0.25%) conversion of pure pyrene to FA, and the roughly 15-fold larger charge of pyrene in the pyrene experiments versus those with soil plus pyrene and sand plus pyrene (Table 1), FA may have also formed during pyrolysis of soil plus pyrene or sand plus pyrene, but gone undetected.

***Determinations of bioactivity* in vitro.** Gentest Corp. (Woburn, MA) tested DCM CF extracts from 500°C and 1,000°C heating of pyrene, pyrene plus sand, and pyrene plus soil, and the DCM extract of the residue from heating uncontaminated soil at 250°C *in vitro* for mutagenic activity at the thymidine kinase locus in h1A1v2 human diploid lymphoblasts using a 72-hr exposure. The procedure has been described elsewhere (*17,35*). Most, if not all, of these seven samples are mixtures of two or more PAHs and may contain other organic compounds that can not be detected with our analytical equipment. Bioassays of whole mixtures are informative, although appreciably more testing would be needed to elucidate which mixture components cause bioactivity. This is because interactions among mixture components may amplify or inhibit the mutagenic potency of individual compounds. (To test for such effects would require numerous bioassays, i.e., of all the compounds individually and of component mixtures to simulate the various permutations and combinations of PAH interactions in the whole mixtures.) Before testing, we exchanged the DCM solvent and redissolved a known mass of

**Table 4.** CPP yields (percent of original pyrene) from heating pyrene-contaminated soil or controls in a tube furnace.[a]

| | Temperature (± 20°C) | | |
|---|---|---|---|
| Material[b] | 500°C | 750°C | 1,000°C |
| Pyrene | ND | ND | 0.30 |
| Soil + pyrene | ND | < 0.54[c] | < 5.55[c] |
| Sand + pyrene | ND | ND | < 5.03[c] |

ND, none detected.
[a]Estimates based on relative peak areas and gravimetrically determined extractables yields; CPP was detected only in the CF condensate (i.e., not in the extract of the heated soil residue). [b]No PAHs were detected in the extractables (residue and CF) from heating uncontaminated soil or uncontaminated sand. [c]The real value is lower due to coelution of a pyrene derivative with CPP.

**Table 5.** BaP yields (percent of original pyrene) from heating pyrene-contaminated soil or controls in a tube furnace.[a]

| | Temperature (± 20°C) | | |
|---|---|---|---|
| Material[b] | 500°C | 750°C | 1,000°C |
| Pyrene | ND[c] | ND | ND |
| Soil + pyrene | ND | ND | 0.32 |
| Sand + pyrene | ND | ND | 0.63 |

ND, none detected.
[a]Estimates based on relative peak areas and gravimetrically determined extractables yields; BaP was detected only in the CF condensate (i.e., not in the extract of the heated soil residue). [b]No PAHs were detected in the extractables (residue and CF) from heating uncontaminated soil or uncontaminated sand.

sample in DMSO. Results are presented as the range of concentrations tested plus the smallest concentration, if any, at which the material exhibited statistically significant mutagenic activity (Table 7).

The detection of mutagenicity in the CF extracts from soil plus pyrene and sand plus pyrene at 1,000°C is consistent with our observation of the mutagens CPP (Table 4) and BaP (Table 5) in these specimens. Similarly, the absence of mutagenicity in the CF extracts from pyrene and sand plus pyrene at 500°C is consistent with our observation of pyrene (Table 2) as the only PAH in these samples; that is, we found no CPP (Table 4) or BaP (Table 5). The lack of mutagenicity in the 1,000°C CF extract from pyrene is surprising given our detection of CPP in this sample (Table 4). The explanation may be that the mass concentration of CPP (< 0.89 wt%) is too low to be detected in the mutagenicity assay. The absence of mutagenicity in the CF extract from the 250°C residue of uncontaminated soil is consistent with the absence of PAHs in this sample (Table 2). The mutagenicity of the CF extract from 500°C heating of soil plus pyrene (Table 7) cannot be explained by CPP and BaP, neither of which were detected in this sample (Tables 4 and 5). Pyrene and a small weight fraction of pyrene derivatives identified essentially as pyrene molecules substituted with alkyl groups were the only PAHs detected in this sample (Table 2). We do not know if these pyrene derivatives have been tested for mutagenicity in this assay. A possible correlation between mutagenicity and methyl group substitution has been suggested for alkyl derivatives of other PAHs, that is, phenanthrene, fluoranthene, and chrysene (*17*). Thus, the pyrene derivatives detected here cannot be ruled out as a source of the mutagenicity detected for the soil plus pyrene CF extract at 500°C. Tables 2 and 7 reveal no counterexamples, that is, the presence of pyrene derivatives in samples showing no mutagenicity. If some of the pyrene derivatives are mutagenic, they may also be contributing to the mutagenicity in the soil plus pyrene CF extract at 1,000°C (Tables 2 and 7).

**Table 6.** Comparison of PH and CPP yields at 1,000°C ± 20°C.[a]

| Substrate | Percent of initial pyrene | |
|---|---|---|
| | PH yield[b] | CPP yield[b] |
| Pyrene | 0.32 | 0.30 |
| Sand + pyrene | 0.26 | < 5.03[c] |
| Soil + pyrene | 0.31 | < 5.55[c] |

PH, phenanthrene.
[a]PH and CPP were detected only in the CF condensate, not in the extract of the heated soil residue. [b]Recovered from CF by extraction with methylene chloride. [c]The real value is lower due to coelution of a a pyrene derivative with CPP.

## Discussion

The present experiments have been conducted under relatively well-controlled conditions at a small scale and do not expose soil, contaminants, or their reaction products to exogenous oxygen. In particular, roughly 20 g of a Superfund-related soil matrix contaminated with about 5 wt% pyrene were heated in a porcelain combustion boat within a tube furnace under a flow of helium gas for 45–60 sec. Thus, our technique in this study is not designed or intended to forecast the extent of soil or by-product cleaning attainable in practical-scale soil remediation technologies in which thermal treatment is followed by high temperature oxidation and/or other cleaning measures (e.g., adsorption on activated carbon). Nevertheless, the present findings are relevant to current and potential commercial practice. Studies under oxygen-free conditions (at any scale) provide a base case against which to differentiate $O_2$-induced effects. Further, they help diagnose and interpret off-specification performance of oxidative systems when desired oxygen potentials are vitiated (e.g., because of mixing imperfections, temperature excursions, under-feeding of oxidant, or overfeeding of soil). They also help elucidate the behavior of nonoxidative technologies, for example, heating in thermal plasmas or baths of molten material.

This study elucidates effects of treatment temperature and soil-contaminant interactions on decontamination efficiency and on product yields, identities, and mutagenicity. Tests were performed at 250, 500, 750, and 1,000°C, but only one temperature, 750°C, cleaned the soil of pyrene and of other DCM extractables. Heating at 250 and 500°C left soil residues containing 61 and 10%, respectively, of the original pyrene as well as other DCM extractables (36 and 25% of the initial pyrene, respectively) including alkylated pyrenes. Heating at 1,000°C gave 100% pyrene removal, but recontaminated the soil with non-PAH DCM extractables. The residues from heating soil plus pyrene at 250, 500, and 1,000°C were contaminated with substances that were sufficiently nonvolatile to remain with the soil at the prevailing treatment temperature; yet these substances were not so tightly bound to the soil to be immune to DCM extraction at near room temperature. At 250, 500, 750, and 1,000°C, the volatilized products of soil cleaning contain pyrene and other PAHs, which at ≥ 500°C diversify in composition with increasing temperature. These PAHs include CPP at 750 and 1,000°C and BaP at 1,000°C. Both compounds exhibit mutagenicity *in vitro* (*17,33*), and BaP is biochemically linked to human lung carcinoma (*34*). *In vitro* human cell tests confirmed the presence of mutagenicity in the volatiles from thermal treatment of soil plus pyrene and sand plus pyrene at 1,000°C. These tests also detected human cell mutagenicity in the volatile effluent from heating soil plus pyrene at 500°C, which was apparently caused by pyrene conversion to pyrene derivatives (alkyl-substituted pyrene). Thus, pyrene was never completely eradicated from the volatiles at any of the four tempertatures, and some pyrene was always converted to other PAHs (Table 2). Further, the removal of all pyrene and other DCM extractables from the soil residue at 750°C still generated volatile PAHs, including at least one mutagen (CPP) and possibly others, i.e., alkylated pyrenes (Table 2).

Mechanistic studies of PAH formation in flames (*36*) suggest possible pathways for the generation of CPP, BaP, and other by-product PAHs in the present experiments. CPP and BaP can be formed by addition of $C_2$ moieties to pyrene. Potential $C_2$ sources are $C_2H_2$ from *a*) soil decomposition, and *b*) pyrene decomposition to equimolar quantities of $C_2H_2$ and PH. If all PH comes from *b*), then PH, provided it undergoes no further reaction, is a proxy for $C_2H_2$ from *b*). Table 6 shows that there is probably sufficient $C_2H_2$ from *b*) to account for the observed CPP yield from neat pyrene at 1,000°C (Table 4). (The data in Table 6 are mass yields. Because the MW of CPP exceeds that of PH, less mass of PH is needed to match 1 mol CPP.) However, much higher CPP yields are seen from soil plus pyrene and sand plus pyrene at 1,000°C, but PH yields are similar to those from neat pyrene. Thus, for soil plus pyrene and sand plus pyrene at 1,000°C, a source of considerably more $C_2H_2$ would be needed to attribute CPP formation to a reaction of

**Table 7.** Mutagenic activity at the thymidine kinase (tk) locus in h1A1v2 cells.

| Sample | Description | Temperature ± 20°C | Extract tested | Concentrations tested (g/mL) | Smallest concentration with mutagenic effect (g/mL) |
|---|---|---|---|---|---|
| 2 | Pyrene | 500 | CF | 0.10, 0.30, 1.0 | Not mutagenic |
| 4 | Pyrene | 1,000 | CF | 0.05, 0.15, 0.50 | Not mutagenic |
| 5 | Uncontaminated soil | 250 | Residue | 0.28, 0.85, 2.8 | Not mutagenic |
| 10 | Soil + pyrene | 500 | CF | 0.10, 0.30, 1.0 | 0.30 |
| 12 | Soil + pyrene | 1,000 | CF | 0.01, 0.03, 0.057, 0.10, 0.17, 0.57 | 0.057 |
| 14 | Sand + pyrene | 500 | CF | 0.1, 0.3, 1.0 | Not mutagenic |
| 16 | Sand + pyrene | 1,000 | CF | 0.01, 0.03, 0.10 | 0.10 |

pyrene with $C_2H_2$, or both soil and sand must stimulate PH destruction. Pyrolysis of this soil matrix does generate $C_2H_2$ (*7*). However, the maximum yield reported by Bucalá et al. (*7*) [i.e., 0.0162 wt% of soil (from heating at 1,000°C/sec to 1033°C and holding for 5 sec before beginning cool-down)] would not provide sufficient $C_2H_2$ to match the CPP yield from soil plus pyrene at 1,000°C. Obviously, heating sand itself gives no $C_2H_2$ because sand contains no carbon. Yet similar yields of CPP (Table 4) and of BaP (Table 5) were observed from heating sand plus pyrene and soil plus pyrene at 1,000°C. In light of these observations, we conclude that $C_2H_2$ addition to pyrene is an important pathway for production of CPP and BaP when heating soil plus pyrene or sand plus pyrene at 1,000°C, and that pyrene itself is a major and perhaps the dominant source of that acetylene. The CPP yield from soil plus pyrene at 750°C (Table 4) was small. Soil pyrolysis may have provided some of the $C_2H_2$ for its production from pyrene [PH, our putative marker for pyrene-derived acetylene, was not detected (Table 2)]. This soil matrix is rich in silica (~ 31 wt%). Further, CPP yields from soil plus pyrene and sand plus pyrene at 1,000°C were similar and also much higher than from pyrene at this temperature (Table 4). These findings suggest that silica may stimulate CPP formation from pyrene, for example, by catalysis of pyrene reactions with $C_2H_2$ or catalysis of $C_2H_2$ production via soil pyrolysis (*7*) or via pyrene conversion to PH. Silicon dioxide may also catalyze PH destruction at this temperature.

Pyrene derivatives, pyrene molecules substituted with short aliphatic hydrocarbon chains, were detected in the residues from heating soil plus pyrene at 250 and 500°C and among the volatile PAHs from heating soil plus pyrene at 250, 500, 750, and 1,000°C (Table 2). A possible formation pathway is pyrene substitution by light aliphatic hydrocarbon gases generated by soil pyrolysis and/or by pyrene decomposition. Pyrene derivatives were not detected when neat pyrene was heated. For sand plus pyrene, they were detected in traces in the 250°C residue extract and in the 750°C CF extract in yields (2.8 wt% of initial pyrene) comparable to those from soil plus pyrene (5.8 wt%). These observations imply that some property of soil that is missing from pyrene and sand can enable or augment pyrene alkylation at 250, 500, and 1,000°C. Some possible properties are a nonsilica mineral or soil pyrolysis products. Pyrolysis of this soil matrix at 1,000°C/sec generates methane, ethane, ethylene, and $C_2H_2$ in yields that increase as temperature increases from 350 to 1,050°C (*7*), but which are always small [i.e., < 0.09, < 0.006, < 0.05, and < 0.02 wt% of soil, respectively (*7*)].

We detected bipyrenyls in the CF extracts from pyrene and sand plus pyrene at 750 and 1,000°C, but bipyrenyls were detected only at 1,000°C in soil plus pyrene (Figure 2). In light of the work of Mukherjee et al. (*16*), we postulate that these PAHs are formed by pyrene dimerization. Cyclodehydrogenation can then begin a complex growth process, which culminates in soot. The stark differences in the bipyrenyl yields at 750°C for the three substrates and the differences in how those yields change when temperature is increased to 1,000°C (Figure 2) suggest that silica may catalyze bipyrenyl formation at 750°C and bipyrenyl consumption at higher temperatures. Figure 2 suggests that for soil plus pyrene other pathways displace pyrene conversion to bipyrenyls at temperatures of < 750°C. A plausible competing reaction is the formation of pyrene derivatives by reactions of pyrene with light gases evolved by soil or pyrene pyrolysis, as discussed above.

## Conclusions

For oxygen-free heating of a pyrene-contaminated Superfund-related soil matrix in a laboratory scale tube furnace at 250–1,000°C, thorough decontamination of the soil residue was realized only at 750°C. By "thorough," we mean complete pyrene removal and absence of PAHs or other methylene chloride extractables in the soil residue. However, all treatment temperatures resulted in volatile PAH by-products that contain pyrene, that increase in compositional diversity with increasing temperature from 500 to 1,000°C, and that include bioactive PAHs at higher temperatures, for example, CPP at 750°C and CPP and BaP at 1,000°C. Results from *in vitro* human cell testing included mutagenicity in volatile products from heating pyrene-contaminated soil at 500 and 1,000°C. Further, even severe heating of soil contaminated with a nonmutagen (to 500°C, which is well above the contaminant's boiling point) can produce soil residues still befouled by the original pollutant, by other PAHs, and potentially by mutagenicity. Both literature and the present results suggest the following as plausible pathways for pyrene conversion to higher MW PAHs, including mutagens, when pyrene-contaminated soil is heated to final temperatures of 250–1,000°C: *a*) reaction with light gases, such as soil- or pyrene-derived $C_2H_2$ to form alkylated pyrenes as well as BaP and CPP; *b*) loss of $C_2$-units followed by reaction with a PAH to form, for example, a five-membered ring species such as CPP, or, via two further reactions, to form a six-membered ring leading to BaP; and *c*) dimerization to form bipyrene isomers, followed by cyclodehydrogenation leading to MW growth and ultimately (at 1,000°C) soot. The relative impacts of *a*) to *c*) are affected by temperature and to some extent by pyrene-soil interactions. At 1,000°C, yields of CPP and BaP are considerably higher when heating soil plus pyrene and sand plus pyrene than from heating pyrene alone; this suggests a significant role for the soil (which is silica rich) in generating these two mutagens from pyrene (e.g., silica catalysis of $C_2H_2$ production from pyrene). Reactions with light gases are plausible at all temperatures, assuming there are adequate inventories of these gases. Loss of $C_2$-units from pyrene becomes more important at higher temperatures and may be augmented by silica in the soil (e.g., by heterogeneous catalysis). PAH dimerization reactions have been detected for neat pyrene and sand plus pyrene at 750 and 1,000°C, but only at 1,000°C for soil plus pyrene, suggesting a possible role for silica in bipyrene formation and consumption (Figure 2). Our data on PAH compositions and mutagenicity show that by-products of environmental health interest can be formed during thermal treatment of soil contaminated with a nonmutagen (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, for example, by further heating, oxidation, or adsorption on solids.

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