Decommissioning Samples From the Ft. Lewis, WA, Solvent Refined Coal Pilot Plant: Chemical Analysis and Biological Testing

**W. C. Weimer
C. W. Wright**

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DECOMMISSIONING SAMPLES
FROM THE FT. LEWIS, WA
SOLVENT REFINED COAL PILOT
PLANT: CHEMICAL ANALYSIS
AND BIOLOGICAL TESTING

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Pacific Northwest Laboratory
Richland, Washington 99352

FOREWORD

This report presents the results from chemical analyses and limited biological assays of three sets of samples from the Ft. Lewis, WA solvent refined coal (SRC) pilot plant. The samples were collected during the process of decommissioning this facility. Chemical composition was determined for chemical class fractions of the samples by using high-resolution gas chromatography (GC), high-resolution GC/mass spectrometry (MS) and high-resolution MS. Biological activity was measuring using both the histidine reversion microbial mutagenicity assay with Salmonella typhimurium, TA98 and an initiation/promotion mouse-skin tumorigenicity assay.

CONTRIBUTORS

Bioassay

D. D. Mahlum
D. L. Stewart

Chemical Separations

L. M. Lawless
K. A. Loss

Gas Chromatography

B. K. Hayden
R. B. Lucke
C. W. Wright

Mass Spectrometry

E. K. Chess
C. W. Wright

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LIST OF ABBREVIATIONS

AH	= Aliphatic hydrocarbon(s)
amino-PAH	= Amino-substituted polycyclic aromatic hydrocarbon(s)
amu	= Atomic mass units
BaP	= Benzo[a]pyrene
CI	= Chemical ionization
DMBA	= Dimethylbenz[a]anthracene
DMSO	= Dimethyl sulfoxide
DOE	= U.S. Department of Energy
FID	= Flame ionization detector
FOB	= Fuel oil blend
GC	= Gas chromatography
h	= Hour(s)
HD	= Heavy distillate
HP	= Hewlett-Packard
HPAH	= Hydroxyl polycyclic aromatic hydrocarbon(s)
I/P	= Initiation/promotion
ISTD	= Internal standard
min	= Minute(s)
MS	= Mass spectrometry
NBS	= National Bureau of Standards
NPAC	= Nitrogen-containing polycyclic aromatic compound(s)
NPD	= Nitrogen-phosphorus detector
PAA	= Primary aromatic amine(s)
PAH	= Polycyclic aromatic hydrocarbon(s)
PFK	= Perfluorokerosene
PFPA	= Pentafluoropropionic anhydride
PMA	= Phorbol myristate acetate
PNL	= Pacific Northwest Laboratory
ppm	= Parts per million
ppt	= Parts per thousand
P&M Co.	= Pittsburg and Midway Coal Mining Co.
PS	= Process solvent
SP	= Spectra-Physics
SRC	= Solvent refined coal
2-AA	= 2-Aminoanthracene
2-CA	= 2-Chloroanthracene
6-AC	= 6-Aminochrysene

EXECUTIVE SUMMARY

The Pittsburgh and Midway Coal Mining Company operated the solvent refined coal (SRC) pilot plant at Ft. Lewis, WA for 7 years, until September of 1981. The closure and subsequent dismantlement of this plant in 1982-1983 offered a unique sampling opportunity to obtain materials which were not previously available. These materials may be representative of those to which workers at an operating coal liquefaction facility could be routinely exposed. Some of these samples had accumulated on or in pieces of equipment or portions of the pilot plant structure over a number of years; many were exposed to natural environmental weathering processes. Thus, analysis of these samples offered an opportunity to evaluate any environmental transformations which occurred.

Three sets of samples were collected between May 1982 and November 1982. Fifty-eight site samples of scrapings from equipment and structural members of the plant, drippings from beneath valves, and acetone washes of vertical surfaces in common areas were collected in May. In addition, 12 sediment samples from an evaporation pond for treated wastewater were obtained during May. Additional samples (22 total) of coal liquid residues were collected from within the pipes and valves of process equipment at several times during the actual dismantling process.

The site and process equipment samples formed the major portion of the sample set examined in this research. The chemical natures of all of these materials and the biological properties of a few of these samples were compared with some of the product materials that had been produced at this facility, namely, the SRC-II fuel oil blend (FOB), heavy distillate (HD) and SRC-I process solvent (PS) coal liquids. The chemical and biological comparisons made in this manner indicated the changes that have occurred in the samples upon environmental weathering and relate results to materials which have been previously characterized in detail (Wright and Weimer, 1984; Wilson et al., 1984).

Gas chromatography (GC) and GC/mass spectrometry (MS) analyses of the environmentally weathered site samples and the process equipment samples

showed that they resembled the overall chemical composition of SRC-II HD material, one of the products of the pilot plant. The lighter ends of the HD were not present in these pilot-plant decommissioning samples, apparently because they had been volatilized during weathering. The average benzo[a]pyrene (BaP) concentrations in 8 sediment samples of 9 analyzed, in 15 of 16 analyzed site samples, and in all 22 process equipment samples all approximated the BaP concentration found in the HD material. Two differences in chemical composition were identified between the HD and the site or process equipment samples. First, GC/MS analysis of selected samples showed the environmentally weathered samples to contain as yet unidentified polar components not present in SRC-II HD. A second important chemical difference was the low level of amino-substituted polycyclic aromatic hydrocarbons (amino-PAH) present in the environmentally weathered site and process equipment samples; much higher concentrations are generally present in HD material.

Three samples were also selected for analysis in two biological assay systems. The level of residual microbial mutagenicity (Ames test) found in these three environmental samples was low, consistent with the low concentrations of amino-PAH found in these samples. When evaluated with an initiation/promotion (I/P) assay for mouse-skin tumorigenicity, however, the same three samples were determined to be equal in biological activity to that of the SRC-II HD.

INTRODUCTION

In September of 1974, the Pittsburgh and Midway Coal Mining Co. (P&M Co.) began operation of a pilot plant, located at Ft. Lewis, WA, which was built to convert solid coal into a low-ash, low-sulfur coal or into low-sulfur liquid oil. This 50-ton/day (solid-product mode; 30-ton/day when operated in liquid-product mode) pilot plant was sufficiently flexible in its operation to provide all of the necessary engineering data needed for design and construction of a larger-scale demonstration-size plant. The Ft. Lewis plant was operated continuously until September of 1981, when the U.S. Department of Energy (DOE) terminated funding for its operations. Dismantlement of the entire facility began in the summer of 1982 and was completed during the early part of 1983.

The closure and subsequent dismantlement of the Ft. Lewis solvent refined coal (SRC) pilot plant provided a unique opportunity to obtain a wide variety of coal-liquid samples which had not been available during the normal operation of this facility. Some of these samples had accumulated on the surfaces of pieces of equipment over a number of years. These samples originated from coal liquids that contained the chemical constituents to which coal-liquefaction plant workers may have been exposed. In addition, these samples have been influenced by the normal environmental weathering processes caused by air, water and sunlight. Examination of the chemical makeup of these samples may provide an indication of the environmental transformations that occur in coal liquids.

Three sets of samples were collected from the Ft. Lewis SRC pilot plant during 1982. These sets included 58 site samples, 12 sediment samples and 22 process equipment samples. The environmentally weathered site samples were comprised of parking-lot scrapings; equipment scrapings; railing and stairway scrapings; acetone washes of doors, walls and railings; scrapings from equipment support structures; and drippings from beneath valves. The sediment samples were from a treated wastewater evaporation pond. The environmental exposure conditions of these two sets of samples ranged from those that had never been exposed to rain or direct sunlight to those that had received constant exposure. Residues of coal liquids found in the pipes and valves of process

equipment were collected on several occasions during the actual dismantling procedure. These residual process equipment sample materials, obtained from the insides of pieces of piping from all of the operation areas, are thought to represent the types of materials to which workers could be exposed during pipe-cutting replacement operations at a working facility.

The general analytical protocol for all samples was approximately the same. A portion of the sample was dissolved in a solvent (the sediment samples were Soxhlet-extracted with a methylene chloride:methanol mixture) or a series of solvents. The soluble constituents were then fractionated, by atmospheric-pressure column chromatography, into aliphatic hydrocarbon (AH), neutral polycyclic aromatic hydrocarbon (PAH), nitrogen-containing polycyclic aromatic compound (NPAC), and hydroxy-substituted polycyclic aromatic hydrocarbon (HPAH) fractions. Gas chromatographic and gas chromatographic/mass spectrometric analyses were performed on the PAH and NPAC fractions for compound identification and quantitation. These fractions were analyzed in detail since they have been shown to be the most biologically active fractions in coal-derived materials as determined by laboratory bioassays (Later et al., 1982; Wilson et al., 1984; Mahlum et al., 1983, 1984; Later et al., 1983). Selected samples were analyzed for amino-substituted PAH (amino-PAH) content by further fractionation of the NPAC fraction. Amino-PAH have been previously shown to be the determinant mutagens in coal-derived materials (Guerin et al., 1980; Wilson et al., 1980). Chemical class fractions of a limited number of samples were analyzed by probe and high-resolution mass spectrometry (MS). A few selected samples were also examined for their biological activity: three samples were subjected to an initiation/promotion (I/P) mouse-skin tumorigenicity test; and additional samples, or fractions, were analyzed by a histidine reversion bioassay for microbial mutagenicity.

EXPERIMENTAL METHODS

SAMPLE COLLECTION

Wastewater Evaporation-Pond Sediments

Sediment samples from the evaporation pond that received the effluent from the wastewater treatment facilities were collected during June 1982 by representatives of Alsid Snowden and Associates, Professional Engineers, Bellevue, WA. Subsamples were provided to Pacific Northwest Laboratory (PNL) for analysis. Individual core samples were taken from several locations within the pond. Each core sample was split into two or more sections, generally representing the sediments laid down during the pilot-plant operations or the underlying base materials which were present prior to start-up of the pilot plant. A listing of the sediment samples received is given in Table 1.

Site Samples

Throughout the Ft. Lewis pilot plant there were accumulations of coal-liquid residues which had deposited during the 7 years of operation. On 5-28-82, 58 individual samples (ranging from small quantities to approximately 100 g) were collected using stainless-steel spatulas and placed into solvent-washed glass jars capped with aluminum-lined lids. Drippings from beneath equipment valves were also obtained by the same technique. An attempt was made to obtain a diversity of samples from each of the process areas. Table 2 gives a summary of the sample types and the number of samples obtained from the different sample locations. Table 3 gives the description of each of the 58 site samples.

Process Equipment Samples

In addition, on four separate occasions during the dismantling operations, samples (ranging in quantity from approximately 25 to 100 g) were collected from the insides of pieces of process equipment. Although the process lines had been cleansed by P&M Co. prior to closure, residues remained in some

TABLE 1. Sediment Samples From Wastewater Evaporation Pond, Collected During June 1982

Sample Description	PNL Sample Number
Surface to 17" depth	2222-81-04
17" to 22" depth	2222-81-07
Surface to 14" depth	2222-81-03
14" to 20" depth	2222-81-08
Surface to 8" depth	2222-81-01
8" to 12" depth	2222-81-10
Surface to 3" depth	2222-81-05
3" to 8" depth	2222-81-09
Topsoil	2222-81-02
4" to 8" soil	2222-81-12
Surface	2222-81-06
4" soil below blacktop	2222-81-11

sections of the piping and in many of the valves. Twenty-two scrapings from the insides of the pipes and valves from each of the plant process areas were collected into solvent-washed glass jars, using stainless-steel spatulas. Because these residual materials had distinctly different viscosities and physical appearances, as many physically different types of samples were collected from the equipment in each process area as was possible. Table 4 gives the description of each of the process equipment samples.

CHEMICAL ANALYSIS

The chemical analysis protocol for the samples included sample preparation, followed by chemical class fractionation and semiquantitative analysis (by ring size) of selected fractions. Several samples were also selected for quantitative analysis of components in fractions, gas chromatography (GC)/MS,

TABLE 2. Summary of Environmentally Weathered Site Samples

Sample Types	
•	Parking lot scrapings
•	Equipment scrapings
•	Stairway and railing scrapings
•	Acetone rinses of doors, walls and railings
•	Scrapings from support structures
•	Valve drippings

Sample Locations	Number of Samples
• Coal storage	1
• Coal preparation (01 Area)	6
• Dissolution (02 Area)	3
• Drum filtration (03 Area)	11
• Distillation (04 Area)	18
• Distillation tower (D4 Area)	4
• Sandvig belt (04 Area)	6
• Lummus deashing	7
• Wastewater processing	2

direct probe MS and simulated distillation. Further description of each of these steps is given below.

Sample Preparation

The sediment samples were initially air-dried overnight, followed by further drying overnight at 105°C. The dried samples were then ground to pass through a 40-mesh sieve, and 7.50 g were Soxhlet-extracted with 200 ml of 1:2 methanol: methylene chloride (v:v) for approximately 20 h. Extracts were then concentrated by removal of solvent, using a Büchi Rotovapor RE-120 at 40°C prior to chemical class fractionation.

Many of the site scraping samples were dry, solid materials or contained significant amounts of gravel or other insoluble material. Prior to any additional sample work-up, all scraping samples were dissolved in a series of solvents, and the insoluble materials were analyzed no further. The solvents

TABLE 3. Description of Site Samples (Collected on 05-28-82)

Sample Number	Description	Area of Collection ^a
<u>2515-</u>		
007-01	Scrapings from parking lot (behind control room)	--
007-02	Scrapings from recycle slurry/ground coal mixer (third level coal preparation area)	01
007-03	Scrapings from ball race grinder (second level coal preparation area)	01
007-04	Scrapings from door handle near ball race grinder	01
007-05	Scrapings from building support and floor (second level coal preparation area)	01
008-01	Scrapings from railing (ground level coal preparation area)	01
008-02	Acetone wipe of restroom wall (ground level coal preparation area)	01
008-03	Scrapings from concrete piling (6-02) of Dissolver "A"	02
008-04	Scrapings from steel support (stripper tower)	02
008-05	Scrapings from concrete pad, "bottoms" sampling location (stripper tower)	02
009-01	Acetone wipe of elevator walls	03
009-02	Scrapings from piling supporting head exchanger near column H-03	03
009-03	Scrapings from BES dryer conditioning drum	03
009-04	Scrapings from outside of door, third level, below spill from a large tank (south side)	03
009-05	Old scrapings from inside railing and stairs leading to third level by pillar 3-03 (north side)	03

^aSee Table 2 for Area descriptions

TABLE 3. (continued)

Sample Number	Description	Area of Collection ^a
<u>2515-</u>		
010-01	Crystalline-like material from valve beside filter feed flash vessel	03
010-02	Scrapings from valve by flash condensate separator (second level)	03
010-03	Scrapings from stairs leading to second level on west end of 03 area, exposed to water and light	03
010-04	Scrapings from pillar and pipe (B-2-09.8) near flare K drum (second level)	03
010-05	Scrapings from pillar beneath filter feed flash vessel (ground level)	03
011-01	Scrapings beneath sampling valve, south side, ground level, exposed to direct sunlight	03
011-02	Scrapings from equipment under vacuum flash feed accumulator (first level)	04
011-03	Scrapings from flush solvent accumulator, beneath major valve works near Sandvig belt area	04
011-04	Scrapings from wash solvent accumulator under sampling valve	04
011-05	Scrapings from stairs and railing, east entrance, Sandvig belt area	04
012-01	Scrapings from stairs and railing, west entrance, Sandvig belt area	04
012-02	Scrapings from upper ladder railing, west entrance, Sandvig belt area	04
012-03	Acetone wipe of railing, Sandvig belt area	04
012-04	Scrapings from ladder in front of column B-04	04

^aSee Table 2 for Area descriptions

TABLE 3. (continued)

Sample Number	Description	Area of Collection ^a
<u>2515-</u>		
012-05	Scrapings from bottom of pedestal at column C-04	04
013-01	Scrapings from ladder to upper floor, west entrance, Sandvig belt area	04
013-02	Scrapings from overhead pipe, Sandvig belt area	04
013-03	Dripping stalactite from upper level grid between columns B-04 and C-04	04
013-04	Scrapings from upper and lower railings between columns B-04 and C-04 (upper level)	04
013-05	Scrapings from 20' off concrete ledge east of column G-04	04
014-01	Scrapings from concrete, taken below sample #2515-013-03	04
014-02	Scrapings from base of pillar F-04	04
014-03	Scrapings from valves under PS accumulator, southeast of column F-04	04
014-04	Scrapings from wheel of valve by column Z-04	04
014-05	Scrapings from bottom railing near accumulation tank area	04
015-01	Scrapings from bottom steps of west staircase in accumulation tank area	04
015-02	Scrapings from top of round vent cover, top floor of tower	04
015-03	Acetone wipe of railing, top floor of tower	04
015-04	Scrapings from top floor or tower	04

^aSee Table 2 for Area descriptions

TABLE 3. (continued)

Sample Number	Description	Area of Collection ^a
<u>2515-</u>		
015-05	Scrapings from beneath sampling valve of seal flush accumulator	04
016-01	Drippings from valve below vacuum flush drum	04
016-02	Scrapings from stairs near vacuum flash condensation drum tank by pillar Z-04	04
016-03	Scrapings from top of vent cover, top floor of tower, south side	04
016-04	Scrapings from bottom of stairs, lower level	Lummus Plant
016-05	Scrapings from pump, lower level	Lummus Plant
017-01	Scrapings under pump on southwest corner, lower level	Lummus Plant
017-02	Scrapings from north platform next to deashing settling tank	Lummus Plant
017-03	Scrapings from base of deashing settling tank	Lummus Plant
017-04	Scrapings from east side floor by deashing settling tank	Lummus Plant
017-05	Acetone wipe of door west of control shed	Lummus Plant
021-03	Scrapings from base of vacuum flash pre-heater, west end	04
021-04	Scrapings from Phoenix tank adjacent to activated sludge tank	Waste Proc.
021-05	Scrapings from tank next to oil/water separator tank	Waste Proc.

^aSee Table 2 for Area descriptions

TABLE 3. (continued)

Sample Number	Description	Area of Collection ^a
<u>2515-</u>		
022-01 ^b	Scrapings from inside Lummus antisolvent deashing unit	Lummus Plant
^a See Table 2 for Area descriptions		
^b Sample collected 11/18/82		

used were methylene chloride and tetrahydrofuran. The weights of the dissolved portion of the samples were determined by the difference in the sample weight before and after dissolution. The samples were concentrated by removal of solvent on a Büchi Rotovapor RE-120 at 40°C and were adjusted to a final volume of 10 ml with methylene chloride prior to chemical class fractionation.

Chemical Class Fractionation

All samples were subjected to chemical class fractionation using atmospheric-pressure column chromatography, according to the method of Later et al. (1980). Briefly, an aliquot of the sample was adsorbed onto 3.0 g of neutral aluminum oxide (Brockman activity I; 80-200 mesh) and air-dried. This was then wet-packed with hexane onto the top of a column containing 9 g of similar neutral alumina. This final column configuration was eluted sequentially with hexane, benzene, chloroform:ethanol (99:1), and tetrahydrofuran to yield four fractions: AH, neutral PAH, NPAC and HPAH, respectively.

An additional fractionation of the NPAC fraction was performed for selected samples. This fraction was separated on a column of silicic acid (Mallinckrodt; 100 mesh) into carbazole, amino-PAH-enriched, and azaarene fractions, using hexane:benzene (1:1), benzene, and benzene:ethyl ether (1:1), re-

TABLE 4. Description of Process Equipment Samples

Sample Number	Description of Equipment from which Sample was Collected ^a	Area of Collection ^b	Date Collected
<u>2515-</u>			
018-01	3-in.-diameter valve	04	08/13/82
018-02	2-in.-diameter valve	04	08/13/82
018-03	2½-in.-diameter valve	03	08/13/82
018-04	3-in.-diameter valve	03	08/13/82
018-05	3-in.-diameter valve (black frosting)	03	08/13/82
019-01	Pump	04	08/13/82
019-02	Pump	03	08/13/82
019-03	3-in.-diameter valve	03	08/23/82
019-04	3-in.-diameter valve (black frosting)	03	08/23/82
019-05	3-in.-diameter valve (very viscous and dry)	03	08/23/82
020-01	2½-in.-diameter valve (very viscous)	03	08/23/82
020-02	Overhead pipe (soft and crumbly)	03	09/02/82
020-03	Large valve (dry and crumbly)	03	09/02/82
020-04	Large valve (black goo)	03	09/02/82
020-05	Small valve (hard and semiwet)	04	09/02/82
022-02	Stainless-steel pipe	01	11/18/82
022-03	Valve	Unknown	11/18/82
022-04	4-in.-diameter valve	Unknown	11/18/82
022-05	2-in.-diameter stainless-steel pipe	01	11/18/82
023-01	Holes in distribution pipe	01	11/18/82

^aUnusual sample characteristics are noted in parentheses.

^bSee Table 2 for Area descriptions

TABLE 4. (continued)

Sample Number	Description of Equipment from which Sample was Collected	Area of Collection ^a	Date Collected
<u>2515-</u>			
023-02	Stainless-steel pipe in antisolvent area	Lummas	11/18/82

^aSee Table 2 for Area descriptions

spectively. A diagram of the chemical class fractionation steps is shown in Figure 1.

Semiquantitative Analysis of PAH and NPAC Fractions

All PAH and NPAC fractions were screened by high-resolution GC to estimate the percent composition of two-, three-, four-, five- and six-ring-and-larger components. The results of this screening were used to select samples for quantitative GC analysis and qualitative GC/MS analysis. Fractions were chromatographed on a Hewlett-Packard (HP) 5880A gas chromatograph equipped with dual J&W DB-5 fused silica columns; each was 25 m x 0.25 mm ID, 0.25 μ m film thickness. The dual columns allowed the simultaneous detection of components by two detectors as described by Wright (1984). Quantitation was performed with a flame ionization detector (FID); a nitrogen-phosphorus detector (NPD) was used to monitor the breakthrough of nitrogen compounds into the PAH fraction and to characterize the NPAC fraction. Temperature-programming was selected to optimize the separation of four-, five- and six-ring components in a National Bureau of Standards (NBS) coal-tar sample. The temperature program was isothermal at 50°C for 2 min, heating at 10°C/min to 130°C, heating at 3°C/min to 202°C, heating at 4°C/min to 300°C and isothermal for 10 min.

Analyses were performed using the external standard method. Percent composition of ring sizes in the total dissolved samples was determined using area summation, in which a total area was obtained for the two-, three-,

FIGURE 1. Chemical Class Fractionation Procedure

four-, five- and six-ring-and-larger components. The summation times used for these area-percent determinations were obtained from the retention times of 80 known components in an NBS coal-tar sample. The response factor for a given ring-size region was determined from the average response factor of a mixture of standards from multilevel calibrations for that ring-size region.

The number of NPAC standards available was limited; therefore, the PAH standard calibration mixture was used for both the PAH and NPAC fractions. Thus, the data obtained from the analysis of these NPAC fractions are useful only for sample-to-sample comparisons.

Quantitative Analysis of PAH and NPAC Fractions

High-resolution GC was used to determine, quantitatively, the levels of some 70 compounds in the PAH and NPAC fractions from the decommissioning samples. An HP 5880A gas chromatograph equipped with a 25-m x 0.25-mm ID fused-silica capillary column coated with DB-5 (J&W Scientific) and FID was used. The oven was temperature-programmed from 50 to 300°C at 3°C/min. Helium carrier gas was used with splitless injection. Quantitative results for the fractions were determined by average-response factors of standards calculated for seven concentrations ranging from 5 to 400 µg/ml. When standards for specific components were not available, the response factors for compounds of the same chemical class with similar retention times were substituted.

2-Chloroanthracene (2-CA) was added as an internal standard (ISTD), with fractions quantified at a concentration level of 5 mg/ml. Identification of components quantified was determined by retention time and retention index measurements (Lee et al., 1979). Amino-PAH compounds were quantified by high-resolution GC analysis using the pentafluoropropionic anhydride (PFPA) derivatized amino-PAH-enriched fractions according to the methods of Later, Lee and Wilson (1982). The 2-CA was added as an ISTD standard at a final concentration of 250 ng/µl. Response factors were calculated from derivatized standard amino-PAH compounds. An HP 5880A GC, equipped with an electron capture detector, was used with other chromatographic conditions identical to those previously described.

Gas Chromatography/Mass Spectrometry (GC/MS)

A limited number of the PAH and HPAH fractions isolated from several samples were analyzed by GC/MS. Samples selected for analysis were: 1) those used for I/P mouse-skin tumorigenesis (see later section for discussion); 2) those representative of samples that contained high concentrations of unidentified components that eluted in the five- to six-ring PAH region of the gas chromatogram; and 3) those that were representative of samples that contained a high proportion of HPAH. Details of the samples that were analyzed are given listed in Table 5.

The GC/MS analyses were performed on an HP 5982A quadrupole mass spectrometer interfaced to an HP 5710 gas chromatograph equipped with a 15-m x 0.25-mm ID fused-silica capillary column coated with DB-5 (J&W Scientific). The oven was temperature-programmed from 50 to 300°C at 8°/min. Splitless or on-column injection techniques were used as noted. The GC transfer line was modified so that the fused silica column was inserted to within 5 to 10 mm of the ionizing electron beam in the ion source. The quadrupole was operated in the electron-impact mode at 70 eV with a typical scan rate of 100 atomic mass units (amu) per second. Spectra were acquired and processed by an HP 5934A data system.

Direct-Probe MS

A limited number of chemical class fractions were analyzed by probe and high-resolution MS. Five µl of the PAH fraction isolated from sample #2515-016-01 and the HPAH fraction from sample #2515-009-03, diluted to 5 and 10 mg/ml in benzene, respectively, were analyzed by low-voltage MS, utilizing a probe for sample introduction. A VG-ZAB-1F mass spectrometer operated at 10 eV with a 6-kV accelerating voltage was used. The sample probe was brought from ambient to 250°C while scanning a mass range of 60 to 500 amu. The dynamic mass resolution was 1:2000, and the source temperature was 250°C. Data were acquired and processed by a VG 2035 data system.

Unknown components of certain masses were analyzed further by high-resolution MS for elemental composition. A decade-resistance peak-matching unit was used in conjunction with the VG-ZAB-1F mass spectrometer for the peak-

TABLE 5. Samples Analyzed by GC/MS

Sample Number	Source	Process Area ^a	PAH Fraction	HPAH Fraction
2515-007-05	Scrapings from building support structure and from floor (second level of coal preparation area)	01	X	X
2515-009-03	Scrapings from outside of conditioning drum	03	X	X
2515-009-05	Weathered scrapings from north side of railing and stairs leading to third level	03	X	X
2515-011-01	Scrapings from beneath exterior sampling valve, south side, ground level, exposed to sunlight	03	X	X
2515-014-01	Scrapings from concrete support, below columns B-04 and C-04	04	X	X
2515-015-02	Scrapings from top of round vent cover, top floor of tower	04	X	-
2515-016-01	Drippings from valve below vacuum flash drum	04	X	-

^aSee Table 2 for area description

matching analysis. Perfluorokerosene (PFK) was used as the mass standard. The static mass resolution was 1:10,000.

Simulated Distillation

Simulated distillation analysis was performed on a few, selected site samples to compare the boiling ranges of these materials with those of the

SRC-II heavy distillate (HD) and the SRC-I process solvent (PS) samples. This analysis was a determination of percent of sample distilled versus temperature and was performed with a gas chromatograph, per ASTM D-2887, "Boiling Range Distribution of Petroleum Fractions by Gas Chromatography." GC separation was carried out on a 2-ft glass column packed with 3% OV-1 on 100/120-mesh Gas Chrom Q, using helium as a carrier gas. An HP 5700 GC equipped with an FID was used. Oven temperature was initially 50°C and was held for 2 min prior to an increase of 8°C/min to 260°C, which was held for 8 min. Analysis of the data was performed on a Spectra-Physics (SP) 4100 computing integrator, using the SP simulated-distillation program "SDGAS1" and the calibration program "SDCAL1." Naphthalene, fluorene, phenanthrene, fluoranthene and chrysene were used as standards for calibration.

BIOLOGICAL ANALYSIS

Microbial Mutagenicity Assay

Standard agar-plate mutagenicity assays were performed as described by Ames et al. (1975), using a Salmonella typhimurium, TA98 microbial tester strain with dimethyl sulfoxide (DMSO) as the carrier solvent. Standard amounts of 2-aminoanthracene (2-AA), benzo[a]pyrene (BaP) and a complex basic fraction from SRC-II HD were tested with Aroclor-induced rat liver (S9) homogenates used for metabolic activation. The optimum levels for S9 were established and monitored daily during the experiments. Negative controls included the Salmonella test strain with and without microsomal enzymes. Revertant colonies per petri dish were counted electronically using a Biotran II automated colony counter.

The specific activity of the tested materials was expressed as revertant colonies of S. typhimurium, TA98/μg of test material. A positive test response was one in which the maximum mutagenic response was twofold or greater than the background response (in revertant colonies). The mutagenic potency was estimated by a linear-regression analysis of the dose-response data. The criteria used for selecting the optimum dose range for estimating a linear dose response for a given material are as follows: at least a four-point dose range, approximate doubling of response for a doubling of dose concentration;

a correlation coefficient of 0.8 or greater for the regression analysis; and an intercept on the response axis that was within 20% of that for the negative control for the day.

I/P Mouse-Skin Tumorigenicity Assay

Three environmentally weathered samples that had relatively high concentrations of four-ring and larger PAH components were tested for their initiating ability in mouse-skin carcinogenicity. These were samples #2515-009-03, #2515-011-01 and #2515-016-01. Previous work by Calkins et al. (1981) and Mahlum (1983a) has demonstrated the effectiveness of I/P studies in predicting the mouse-skin carcinogenicity potential of coal-derived liquids.

Female, C0-1 mice (Charles River, Portage, MI) approximately 6 weeks of age were used for this study. They were housed five per cage on standard bedding material (Sani-Cel, Paxton Processing Co., Paxton, IL) with food (Wayne 4% Lab-Blox, Allied Mills, Libertyville, IL) and tap water available ad libitum. Prior to administration of the test materials, the animals were ear-tagged for unique identification, weighed, shaved, and assigned to a test group of 28 to 30 animals per group. Each test material was diluted 1:1 with acetone, and 50 μ l of diluted material was applied to the shaved backs of the mice. The resulting dose was approximately 25 mg of crude test material per mouse. Two groups of animals were initiated with 50 μ g of dimethylbenz[a]anthracene (DMBA; Eastman Chemical Co.) or BaP (Sigma Chemical Co.) to serve as positive controls. Beginning 2 weeks after initiation, 5- μ g doses of phorbol myristate acetate (PMA; Sigma Chemical Co.) were applied to the initiated area twice weekly for a period of 6 months. The mice were shaved as necessary throughout the study, usually once per week. Animals were observed regularly for tumor growth. Approximate tumor location and size were sketched each week to note progression of papilloma development.

RESULTS AND DISCUSSION

SITE AND PROCESS EQUIPMENT SAMPLES

The 58 site samples were representative of: 1) coal-liquid residuum from each of the operational areas of the pilot plant; 2) all possible degrees of environmental exposure to air, light, and water; 3) varying durations of environmental exposure; 4) materials to which the plant workers may have received exposure; and 5) samples from the aqueous-waste-treatment area. The additional 22 samples obtained from pieces of process equipment during the actual plant dismantling operations were considered representative of those materials to which workers may have been exposed during such maintenance operations as pipe-cutting, welding, and valve replacement. Results follow for the chemical analysis of the site and process equipment samples and for the biological testing of a limited number of site samples. Comparisons of these samples with some of the product materials that were produced at this facility are given.

Sample Dissolution

The sample dissolution steps (already described) that were used to separate the inert mineral matter in the site samples from the coal liquid residuum generally solubilized one-third to one-half of the sample, as indicated in Table 6. Nearly complete solubilization was achieved for a few of the samples. Approximately the same proportion of each of the process equipment samples was also solubilized by this dissolution procedure (Table 7), although these samples generally did not contain as much inert material as the site samples. Only the fractions of the samples which were solubilized by the procedure described above were used for further chemical or biological analysis.

Composition by Chemical Class

The results of the chemical class fractionation of the dissolved site and process equipment samples by atmospheric-pressure alumina chromatography are listed in Tables 8 and 9, respectively. The amounts of material recovered

TABLE 6. Dissolution of Site Samples

Sample Number ^a	Weight Percent of Original Sample Dissolved	Sample Number ^a	Weight Percent of Original Sample Dissolved
2515-007-01	13.6	2515-013-01	48.8
2515-007-02	39.0	2515-013-02	46.8
2515-007-03	51.1	2515-013-03	75.9
2515-007-04	59.8	2515-013-04	78.1
2515-007-05	44.2	2515-013-05	52.3
2515-008-01	38.1	2515-014-01	74.4
2515-008-03	24.3	2515-014-02	59.3
2515-008-04	55.0	2515-014-03	92.0
2515-008-05	29.0	2515-014-04	33.0
		2515-014-05	49.7
2515-009-02	36.4		
2515-009-03	31.7	2515-015-01	38.9
2515-009-04	63.1	2515-015-02	91.5
2515-009-05	29.9	2515-015-04	94.6
		2515-015-05	55.2
2515-010-01	4.0		
2515-010-02	23.2	2515-016-01	71.1
2515-010-03	34.6	2515-016-02	35.5
2515-010-04	30.6	2515-016-03	89.0
2515-010-05	71.0	2515-016-04	51.2
		2515-016-05	80.2
2515-011-01	28.3		
2515-011-02	34.0	2515-017-01	40.4
2515-011-03	61.5	2515-017-02	39.6
2515-011-04	33.4	2515-017-03	88.2
2515-011-05	52.6	2515-017-04	9.3
2515-012-01	54.2		
2515-012-02	51.3	2515-021-03	30.4
2515-012-04	35.1	2515-021-04	37.9
2515-012-05	35.6	2515-021-05	37.7
		2515-022-01	49.8

^aSee Table 3 for description

TABLE 7. Dissolution of Process Equipment Samples

Sample Number ^a	Weight Percent of Original Sample Dissolved
2515-018-01	52.4
2515-018-02	49.6
2515-018-03	26.9
2515-018-04	54.8
2515-018-05	52.1
2515-019-01	30.7
2515-019-02	32.6
2515-019-03	40.7
2515-019-04	47.0
2515-019-05	47.4
2515-020-01	44.9
2515-020-02	41.3
2515-020-03	43.7
2515-020-04	47.9
2515-020-05	26.8
2515-022-02	46.3
2515-022-03	62.7
2515-022-04	47.8
2515-022-05	32.1
2515-023-01	51.7
2515-023-02	84.9

^aSee Table 4 for description

from the columns were generally acceptable; greater than 80% recovery was achieved for the majority of the samples. The average total recovery for all samples was 80.6%. For nearly all the site and process equipment samples, the PAH fraction constituted the largest proportion, averaging 34.2% of the sample and comprising up to 56% of some of the samples. The second largest fraction was generally the NPAC fraction, averaging 23.3% by weight and constituting up to approximately 40% of the sample. The HPAH fractions generally comprised 20% or less of the samples and averaged 18.1%; however, one sample was nearly

TABLE 8. Chemical Class Composition of Dissolved Site Samples^a

Sample Number ^b	Weight Percent Composition				NPAC Plus HPAH	Percent Recovery
	AH	PAH	NPAC	HPAC		
2515-007-01	9.9	43.2	28.2	13.6		94.9
2515-007-02	6.7	42.6	46.2	22.3		117.8
2515-007-03	4.1	47.8	-	-	53.4	104.7
2515-007-04	4.3	31.7	29.6	18.6		90.2
2515-007-05	3.2	41.1	8.6	47.9		100.8
2515-008-01	10.4	40.2	23.8	19.1		93.5
2515-008-02	4.2	24.2	-	-	46.3	74.7
2515-008-03	7.7	30.0	29.8	15.4		82.9
2515-008-04	2.4	40.4	-	-	55.6	98.4
2515-008-05	4.1	30.9	-	-	63.1	98.1
2515-009-01	3.3	10.6	-	-	48.4	62.5
2515-009-02	4.2	16.7	-	-	34.2	55.1
2515-009-03	4.0	38.8	27.8	39.5		110.1
2515-009-04	1.7	29.5	33.0	26.5		90.7
2515-009-05	3.2	27.0	-	-	42.0	72.2
2515-010-01	0.9	9.1	-	-	19.5	29.5
2515-010-02	4.2	21.3	-	-	33.0	58.5
2515-010-03	3.9	33.6	-	-	31.5	69.0
2515-010-04	3.7	28.6	-	-	32.4	64.7
2515-010-05	1.2	37.5	-	-	50.8	89.5
2515-011-01	4.1	34.7	21.1	29.9		89.8
2515-011-02	3.1	47.1	21.6	28.2		100.0
2515-011-03	8.0	34.3	22.5	14.2		79.0
2515-011-04	4.0	35.1	19.1	14.6		72.8
2515-011-05	2.2	35.4	31.5	24.9		94.0
2515-012-01	3.9	33.1	31.3	23.1		91.4
2515-012-02	5.1	33.5	23.4	27.8		89.8
2515-012-03	1.6	18.3	33.5	10.5		63.9
2515-012-04	4.2	36.0	23.9	16.8		80.9
2515-012-05	6.9	35.8	25.3	22.2		90.2
2515-013-01	4.5	34.6	30.3	27.1		96.5
2515-013-02	3.6	30.6	31.9	11.6		77.7
2515-013-03	2.6	32.0	28.7	18.9		82.2

^aData are averages of two or three replicate analyses.^bSee Table 3 for description

TABLE 8. (continued)^a

Sample Number ^b	Weight Percent Composition				NPAC Plus HPAH	Percent Recovery
	AH	PAH	NPAC	HPAC		
2515-013-04	8.6	24.8	28.9	25.2		87.5
2515-013-05	4.6	30.4	30.1	27.3		92.4
2515-014-01	5.3	30.2	23.2	32.8		91.5
2515-014-02	4.4	32.8	32.0	18.2		87.4
2515-014-03	10.4	27.3	17.9	12.4		68.0
2515-014-04	5.7	30.4	23.3	16.0		75.4
2515-014-05	4.4	34.0	23.7	14.5		76.6
2515-015-01	5.4	39.2	23.2	26.6		94.4
2515-015-02	3.6	36.3	19.4	12.8		72.1
2515-015-03	1.2	25.1	16.9	10.4		53.6
2515-015-04	4.7	38.8	18.9	14.8		77.2
2515-015-05	3.0	23.8	13.7	8.4		48.9
2515-016-01	1.8	55.9	11.3	9.3		78.3
2515-016-02	5.1	44.2	25.6	21.8		96.7
2515-016-03	1.0	25.9	23.5	21.3		71.7
2515-016-04	4.4	28.0	21.6	21.1		75.1
2515-016-05	5.9	28.2	14.0	19.0		67.1
2515-017-01	11.4	36.1	15.7	15.6		78.8
2515-017-02	3.6	36.5	16.2	15.7		72.0
2515-017-03	3.8	39.2	30.3	14.5		87.8
2515-017-04	3.4	54.4	22.8	18.7		99.3
2515-017-05	1.6	8.9	41.5	13.4		65.4
2515-021-03	3.8	37.0	23.4	24.6		88.8
2515-021-04	5.6	46.4	17.2	14.4		83.6
2515-021-05	8.3	29.0	20.1	15.9		73.3
2515-022-01	6.7	48.2	23.0	13.3		91.2

^aData are averages of two or three replicate analyses.^bSee Table 3 for description

TABLE 9. Chemical Class Composition of Dissolved Process Equipment Samples^a

Sample Number ^b	Weight Percent Composition				Percent Recovery
	AH	PAH	NPAC	HPAC	
2515-018-01	6.5	40.1	19.9	16.3	82.8
2515-018-02	4.3	45.0	21.8	15.8	86.9
2515-018-03	8.4	38.4	31.1	16.4	94.3
2515-018-04	0.7	19.8	4.8	8.9	34.2
2515-018-05	9.9	34.7	20.6	11.9	77.1
2515-019-01	4.8	43.4	23.5	17.1	88.8
2515-019-02	12.3	43.7	25.3	13.4	94.7
2515-019-03	7.0	46.9	26.6	14.5	95.0
2515-019-04	4.3	38.4	22.6	7.5	72.8
2515-019-05	4.9	45.6	19.6	6.0	76.1
2515-020-01	4.1	43.5	22.0	27.7	97.3
2515-020-02	5.5	17.5	0.7	4.4	28.1
2515-020-03	3.3	13.9	3.6	3.4	24.2
2515-020-04	4.7	44.0	6.9	34.0	89.6
2515-020-05	4.9	38.0	28.3	27.6	98.8
2515-022-02	3.7	30.7	29.3	5.9	69.6
2515-022-03	5.3	38.3	30.9	21.8	96.3
2515-022-04	6.0	39.0	34.6	13.8	93.4
2515-022-05	6.7	33.4	15.6	12.2	67.9
2515-023-01	5.3	44.0	31.0	6.3	86.6
2515-023-02	1.9	37.5	19.3	18.1	76.8

^aData are averages of two or three replicate analyses.^bSee Table 4 for description

half HPAH, and several contained about one-third HPAH fraction. The AH fractions averaged 4.8% by weight.

For comparison, the average weight percent composition by chemical class of the SRC products of the Ft. Lewis pilot plant is given in Table 10. The data are for a full-boiling-range (300 to 850°F+) SRC-II coal liquid, SRC-II H0, and SRC-I PS.

TABLE 10. Chemical Class Composition of SRC Materials

Sample	Weight Percent Composition				Percent Recovery
	AH	PAH	NPAC	HPAH	
SRC-II 300 to 850°F+ ^a	13	41	13	16	83
SRC-II HD ^b	7 ± 5	58 ± 7	18 ± 2	15 ± 2	98
SRC-I PS ^c	14	48	14	25	101

^aAverage of three determinations, from Later et al., 1983

^bAverage of more than three determinations, from Wright et al., 1985

^cAverage of two determinations

The site samples appeared, on the average, to have decreased AH and PAH composition and slightly increased NPAC composition compared to the process materials. Chemical class analysis of boiling-point cuts from the full-boiling-range material (Later et al., 1983) indicated that the AH contribution to the total sample decreased dramatically with increasing boiling-point range of the fractions (from 32% in the 300 to 700°F cut to 2% in the 850°F+ cut); the more-polar NPAC fraction increased considerably in these same cuts (from 12 to 35%). The analysis of the site and process equipment samples indicates that the AH and PAH appear to be the most volatile fractions and some evaporation occurs upon extended atmospheric exposure.

Semiquantitative Analysis of PAH and NPAC Fractions

Part of the chemical screening evaluation of all site samples was a semiquantitative analysis of the PAH and NPAC fractions. The purpose of this evaluation was to estimate the relative proportions of four-, five- and six-ring and larger compounds in each of the site samples. Compounds found in the PAH and NPAC fractions have been shown to be the most biologically active materials in coal-derived products as determined by microbial mutagenicity and I/P tumorigenicity in mouse-skin bioassays (Later et al., 1982; Wilson et al.,

1984; Mahlum et al., 1983; Later et al., 1983; Mahlum et al., 1984). In addition, increased biological response has been noted with components of increasing ring size (Mahlum, 1983b; Wright, Later, Dauble and Wilson, 1985).

The data resulting from the semiquantitative GC analyses are listed in Table 11. The four- to six-ring PAH detected ranged from 2.6 to 28.9% of the total composition of the dissolved sample. The detected NPAC composition of four rings or greater ranged from 0.2 to 7.4% of the dissolved sample. When relatively high levels of the larger PAH and/or NPAC components were detected, more-detailed chemical analyses were performed. Additional criteria used for selection of samples for further analysis were as follows: an attempt was made to choose samples from each operational area; some acetone wipes of surfaces that were commonly contacted by workers' hands were analyzed; and samples which, because of their physical location, received high amounts of environmental exposure or no direct exposure to sunlight were selected for further analysis. The 16 samples that received quantitative analysis of the PAH and NPAC fractions are described in Table 12.

Quantitative Analysis of PAH in Selected Samples

The 16 site samples listed in Table 12, as well as eight selected process equipment samples, were analyzed by high-resolution GC. In addition, a subset of these samples was analyzed by GC/MS. The PAH concentration data for the site samples are listed in Table 13; the concentration data for the process equipment samples are given in Table 14.

The principal components of the PAH fractions isolated from all of the site samples were unsubstituted three- and four-ring unsaturated systems. The major constituents were phenanthrene or pyrene, followed by fluoranthene, benzo[b]fluorene, and 2- or 3-methylphenanthrene. The relative concentration of chrysene was elevated in samples #2515-015-02 and #2515-015-03, which were collected from the top of a distillation tower in the 04 Area and received the most concentrated sunlight exposure of any of the samples. This high exposure and resultant temperature increase may have resulted in the distillation of more light-ends materials from these samples than occurred with the other site samples. Using the Mann-Whitney nonparametric test for significance, the

TABLE 11. Semiquantitative Analysis of PAH and NPAC Fractions of Site Samples

Sample Number ^b	Percent Composition: Four-, Five- and Six-Ring Compounds ^a		Sample Number ^b	Percent Composition: Four-, Five- and Six-Ring Compounds ^a	
	PAH	NPAC ^c		PAH	NPAC ^c
2515-007-01	19.75	2.00	2515-013-01	10.44	1.41
2515-007-02	16.67	1.46	2515-013-02	5.61	0.63
2515-007-03	14.94	0.97	2515-013-03	8.37	1.83
2515-007-04	16.88	1.46	2515-013-04	8.40	1.38
2515-007-05	16.80	1.29	2515-013-05	6.81	0.69
2515-008-01	15.79	1.84	2515-014-01	10.41	0.76
2515-008-02	7.69	6.84	2515-014-02	10.12	0.73
2515-008-03	10.75	1.01	2515-014-03	10.32	1.47
2515-008-04	12.20	1.21	2515-014-04	8.70	1.47
2515-008-05	7.24	0.34	2515-014-05	15.06	0.85
2515-009-01	3.56	5.17	2515-015-01	9.82	0.80
2515-009-02	-	0.91	2515-015-02	7.01	1.31
2515-009-03	12.41	1.32	2515-015-03	9.16	2.97
2515-009-04	11.17	1.08	2515-015-04	14.38	1.44
2515-009-05	5.90	0.91	2515-015-05	6.93	1.06
2515-010-01	2.58	0.002	2515-016-01	28.90	0.41
2515-010-02	6.29	0.43	2515-016-02	11.74	-
2515-010-03	10.39	0.61	2515-016-03	15.06	1.34
2515-010-04	8.21	0.21	2515-016-04	9.17	1.60
2515-010-05	11.27	0.65	2515-016-05	7.13	0.96
2515-011-01	13.21	0.74	2515-017-01	15.99	1.48
2515-011-02	12.23	0.92	2515-017-02	15.32	1.34
2515-011-03	24.08	1.31	2515-017-03	20.09	0.50
2515-011-04	11.65	0.54	2515-017-04	14.73	1.68
2515-011-05	11.48	0.35	2515-017-05	3.60	-
2515-012-01	12.97	0.72	2515-021-03	14.59	1.29
2515-012-02	10.08	0.87	2515-021-04	11.85	0.78
2515-012-03	5.44	7.42	2515-021-05	12.15	1.68
2515-012-04	15.66	1.83			
2515-012-05	17.63	1.94			

^aPercent composition determined using area summation and expressed as weight percent of the total dissolved sample

^bSee Table 3 for description

^cBased on responses of PAH standards; therefore, useful only for sample-to-sample comparison

TABLE 12. Description of Selected Site Samples That Received Detailed Chemical Analysis

Sample Number	Description	Area of Collection ^a
<u>2515-</u>		
007-01	Scrapings from parking lot behind control room; sample is coal dust and represents a control sample	--
008-01	Scrapings from railing on ground floor of coal preparation building	01
008-02	Acetone wipe of restroom wall	01
008-04	Scrapings from stripper tower support structure	02
009-01	Acetone wipe of elevator walls	03
009-03	Scrapings from outside of minimum BES dryer conditioning drum; inside building	03
009-05	Scrapings of aged material from inside railing and stairs leading to third level of pillar 3-03, north side of building	03
011-01	Scrapings beneath sampling valve, south side of building, ground level, high exposure to direct sunlight	03
011-03	Scrapings from beneath flush solvent accumulator, near Sandvig belt area	04
012-03	Acetone wipe of railing, Sandvig belt area	04
012-05	Scrapings from bottom of pedestal at column C-04	04
015-02	Scrapings from round vent cover, top floor of distillation tower	04
015-03	Acetone wipe of railing, top floor of distillation tower	04
016-01	Drippings from valve below vacuum flash drum	04

^aSee Table 2 for description

TABLE 12. (continued)

Sample Number	Description	Area of Collection ^a
<u>2515-</u>		
017-03	Scrapings from base of deashing settling tank	Lummus Plant
021-05	Scrapings from tank next to oil/water separator tank	Waste Proc.
^a See Table 2 for description		

ratio of phenanthrene to pyrene was significantly greater (at $\alpha = 0.10$) for all the materials that were sampled from sheltered conditions versus those from unsheltered conditions. This indicated that a higher degree of volatilization occurred in the unsheltered materials, which were in contact with direct sunlight, as compared to the sheltered materials. Additionally, a greater percent of low-molecular-weight materials in the unsheltered materials may have been solubilized and washed away during rainfall conditions.

The data for the eight process equipment samples present essentially the same view of the principal sample constituents as did the site samples. Phenanthrene and pyrene were the two compounds of highest concentration. Sample #2515-019-04 contained a relatively large quantity of acephenanthrylene. The process equipment samples had a significantly higher concentration of lower-molecular-weight components versus pyrene concentration than did either the unsheltered ($\alpha = 0.01$) or sheltered ($\alpha = 0.05$) site samples. In addition, the process equipment samples had a significantly higher ($\alpha = 0.05$) concentration ratio of anthracene to phenanthrene than did the site samples. This indicated that some oxidation of anthracene may have occurred in the samples exposed to the environment, since this represents a relatively easier-to-oxidize PAH compound. (No significant difference was noted for the sheltered versus unsheltered site samples when comparing the ratio of anthracene to phenanthrene.)

TABLE 13. Concentrations of Selected Compounds in PAH Fractions from Selected Site Samples. (Asterisks and R denote replicate sample analyses.)

Compound ^a	Sample Number 2515- (Concentration, ppt)							
	007-01R	008-01R	008-02*	008-04	009-01	009-03R	009-05*	011-01R
Acenaphthene								
Dibenzofuran								
Fluorene	0.30 ^b	0.20		0.80		0.80		0.70
1-Methylfluorene	3.4	6.1	0.40	3.2		3.4	0.90	2.7
Dibenzothiophene	0.30	3.4	0.60	4.3		4.7	1.3	3.8
Phenanthrene	21.1	55.3	8.5	47.0	4.1 ± 0.3 ^c	53.4	40.3	57.9
Anthracene	1.2	2.8		1.8		3.6	2.4	2.7
3-Methylphenanthrene	9.3	14.4	3.7	10.7	1.6 ± 0.1	13.0	12.6	14.0
2-Methylphenanthrene	12.9	19.6	5.4	14.4	2.2 ± 0.1	17.8	16.0	17.9
1-Methylphenanthrene	3.6	4.5	1.6	4.4	1.0	5.2	6.4	5.7
Fluoranthene	8.7	11.6	17.9	17.1	8.2 ± 0.2	24.2	31.9	30.5
Acephenanthrylene	3.6	2.3	1.1	2.9	1.1	2.3	0.70	1.0
Pyrene	44.4	42.0	28.5	33.4	11.5 ± 0.4	42.9	35.0	43.7
Benzo[a]fluorene	4.6	4.4	2.6	1.9	0.6	2.6	3.7	5.0
Benzo[b]fluorene ^d	21.1	18.6	10.5	14.2	3.3 ± 0.3	16.0	8.2	13.9
1-Methylpyrene	4.1	4.3	3.7	4.2	1.6 ± 0.3	4.8	6.8	6.2
Benz[a]anthracene	1.6	1.7	1.5	1.6	0.60 ± 0.05	3.4	4.0	3.3
Chrysene ^e	2.9	2.9	5.6	3.4	2.5 ± 0.3	5.7	5.8	6.1
3-Methylchrysene	1.1	1.2	0.70	1.2	0.5	1.8	2.2	1.5
2-Methylchrysene	6.5	3.3		11.9		3.2	2.8	2.0
6- or 4-Methylchrysene	3.1	2.7	1.4	3.3		2.4	1.3	1.7
1-Methylchrysene	0.40	0.40	0.70	0.40		0.40	0.60	0.20

^aIdentification based on GC retention time and GC/MS data

^bRepresents one determination at 5.0 mg/ml

^cAverage of two determinations at 5.0 mg/ml

^dCo-elutes with 2- or 4-methylpyrene

^eCo-elutes with triphenylene

TABLE 13. (continued)

Compound ^a	Sample Number 2515- (Concentration, ppt)							
	007-01R	008-01R	008-02*	008-04	009-01	009-03R	009-05*	011-01R
Benzo[j or b]fluoranthene	2.0	2.3	1.9	2.9	0.60 ± 0.05	2.7	1.2	1.7
Benzo[k]fluoranthene	0.70	0.90	0.90	1.0	0.20	1.6	0.90	1.1
Benzo[e]pyrene	2.0	1.9	1.3	2.2	0.45 ± 0.05	2.0	0.50	1.0
Benzo[a]pyrene	0.80	0.90		1.4	0.30	1.7	0.70	0.90
Perylene	0.60	0.40		0.60		0.60	0.30	0.30
Indeno[1,2,3-cd]pyrene	2.1	2.1		3.1		1.6	0.60	0.60
Dibenz[a,h or a,c]anthracene				0.60				
Benzo[ghi]perylene	4.2	4.3	1.4	5.2		2.8	0.30	0.90

31 ^aIdentification based on GC retention time and GC/MS data

TABLE 13. (continued)

Compound ^a	Sample Number 2515- (Concentration, ppt)							
	011-03R	012-03	012-05R	015-02	015-03*	016-01*	017-03*	021-05R
Acenaphthene							0.30	
Oibenzofuran							1.5	
Fluorene	0.50		1.2				6.7	0.40
1-Methylfluorene	2.8	0.4	5.6	1.3	1.2	1.6	1.9	4.6
Oibenzothiophene	3.9	1.3	5.0	2.9 ± 0.7	2.9	1.5	1.8	3.5
Phenanthrene	35.5	15.3 ± 1.7	38.6	68.4 ± 15.6	62.8	20.3	124	68.4
Anthracene	2.1	0.5	1.3	1.1	0.40	0.50	5.4	1.5
3-Methylphenanthrene	11.1	5.8 ± 0.4	11.0	12.7 ± 1.1	12.6	4.0	17.8	15.6
2-Methylphenanthrene	14.7	8.3 ± 0.4	15.0	17.9 ± 2.6	18.5	5.6	20.4	19.9
1-Methylphenanthrene	3.8	2.2	3.9	5.1 ± 0.2	5.7	1.1	7.4	5.8
Fluoranthene	15.3	8.5 ± 0.2	8.4	39.1 ± 1.7	41.1	3.9	28.4	29.0
Acephenanthrylene	2.3	1.4	2.4	0.50	1.5	0.40	0.70	1.9
Pyrene	50.7	25.8 ± 1.0	34.6	55.2 ± 4.5	53.7	8.9	32.4	45.0
Benzo[a]fluorene ^b	3.6	2.9 ± 1.3	3.5	4.9 ± 0.8	3.1	4.6	4.0	4.3
Benzo[b]fluorene ^b	23.0	12.6 ± 0.1	18.0	16.8 ± 3.2	14.0	3.1	8.2	15.1
1-Methylpyrene	5.1	2.9 ± 0.4	3.5	6.2 ± 2.0	5.9	0.80	4.6	4.7
Benzo[a]anthracene	3.6	1.8	1.4	3.3 ± 0.5	2.6	0.50	2.2	2.2
Chrysene ^c	4.5	3.4	2.8	8.1 ± 1.3	9.2	0.80	3.7	5.6
3-Methylchrysene	2.3	1.1	1.5	2.1	1.6		1.0	1.2
2-Methylchrysene	1.9		4.4	1.7	3.8	0.30	1.5	1.7
6- or 4-Methylchrysene	2.3	1.7	4.0	2.2	1.5	0.80	1.3	1.2
1-Methylchrysene	0.40	1.0	0.50	0.50	1.1	1.3		0.20
Benzo[j or b]fluoranthene	2.5	1.7	3.0	2.7	3.2	2.5	0.70	1.5
Benzo[k]fluoranthene	1.2	0.8	1.1	1.7	1.8			0.90
Benzo[e]pyrene	2.7	1.7	2.9	1.9	2.4	1.7		1.0

^aIdentification based on GC retention time and GC/MS data

^bRepresents one determination at 5.0 mg/ml

^cAverage of two determinations at 5.0 mg/ml

TABLE 13. (continued)

Compound ^a	Sample Number 2515- (Concentration, ppt)							
	011-03R	012-03	012-05R	015-02	015-03*	016-01*	017-03*	021-05R
Benzo[a]pyrene	1.4	1.1	1.5	1.6	0.80	2.4	0.50	0.50
Perylene	0.70		0.70					0.10
Indeno[1,2,3-cd]pyrene	1.6	1.2	3.0	1.0	1.5			0.50
Dibenz[a,h or a,c]anthracene	0.30							
Benzo[ghi]perylene	3.7	3.4	5.9	1.8	2.3	1.2		1.1

^aIdentification based on GC retention time and GC/MS data

TABLE 14. Concentrations of Selected Compounds in PAH Fractions from Selected Process Equipment Samples. (Asterisks and R denote replicate sample analyses.)

Compound ^a	Sample Number (Concentration, ppt)							
	2515-018-		2515-019-			2515-020-		
	01*	05 & 05* ^b	01 & 01* ^b	04 & 04* ^b	05 ^b	01	02 & 02* ^b	03
Naphthalene			1.36					
2-Methylnaphthalene	0.368	0.642	4.01	0.344				
1-Methylnaphthalene		0.193	0.724					
Biphenyl	1.13	1.87	6.59	0.791	0.390			
1,7-Dimethylnaphthalene	0.317	0.643	1.21	0.595	0.325			
Acenaphthene	1.02	5.01	1.86	3.1	3.52			
Dibenzofuran	1.73	8.29	3.31	3.83	4.56			
Fluorene	11.2	14.0	10.6	12.0	11.9	0.934		
Dibenzothiophene	11.3	9.77	7.54	9.42	10.6	3.49		
Phenanthrene	74.2	82.6	42.9	73.1	78.8	62.0	3.74	0.382
Anthracene	4.83	4.17	2.62	3.39	5.32	2.48		
3-Methylphenanthrene	19.9	10.7	9.05	14.6	13.1	10.5		
2-Methylphenanthrene	20.2	12.3	11.1	14.8	13.7	11.4	0.875	0.408
4-H-Cyclopenta[def]phenanthrene	1.45	2.25		1.00	3.53	2.54		
1-Methylphenanthrene	3.39	3.52	1.78	2.87	3.15	4.4		
Fluoranthene	9.24	22.4	4.42	15.1	25.1	38.1	0.396	0.508
Acephenanthrylene	1.87	2.01	1.43	7.04	1.61	1.88		
Pyrene	62.7	32.8	27.2	39.9	40.9	43.4	0.323	0.471
Benzo[a]fluorene	6.05	6.73	2.23	4.07	6.06	13.5		
Benzo[b]fluorene ^c	31.9	8.04	13.1	18.4	16.0	5.53		0.868
1-Methylpyrene	3.33	2.09	1.35	2.07	2.1	3.95		
Benz[a]anthracene	3.54	2.51	1.29	2.54	3.05	3.69		

^aIdentification based on GC retention time and GC/MS data

^bAverage concentrations of two determinations

^cCo-elutes with 2- or 4-methylpyrene

^dCo-elutes with triphenylene

TABLE 14. (continued)

Compound ^a	Sample Number (Concentration, ppt)							
	2515-018-		2515-019-			2515-020-		
	01*	05 & 05* ^b	01 & 01* ^b	04 & 04* ^b	05 ^b	01	02 & 02* ^b	03
Chrysene ^d	6.31	5.16	2.57	5.25	5.43	7.01		
3-Methylchrysene	2.45	1.28	1.13	1.82	1.53	1.76		
2-Methylchrysene	1.31	0.696	0.621	1.01	0.804	1.02		
6- or 4-Methylchrysene	4.05	1.51	2.21	3.40	2.81	1.05	0.464	0.598
1-Methylchrysene	0.392			0.453				
Benzo[j or b]fluoranthene	4.23	2.29	2.21	3.48	3.04	2.43		
Benzo[k]fluoranthene		0.542						
Benzo[e]pyrene	3.35	1.59	2.02	2.29	1.96	1.14	0.379	0.620
Benzo[a]pyrene	2.10	1.30	1.14	1.50	1.56	1.34	0.590	0.870
Perylene	0.466				0.520			
Indeno[1,2,3-cd]pyrene	1.69	0.764	1.71	1.45	1.00			
0ibenz[a,h or a,c] anthracene								
Benzo[ghi]perylene	3.84	1.18	4.49	2.19	1.66			

^a Identification based on GC retention time and GC/MS data

^b Average concentrations of two determinations

^c Co-elutes with 2- or 4-methylpyrene

^d Co-elutes with triphenylene

The concentrations of the major PAH constituents in the three principal products produced at this pilot plant (Table 15) provide a useful comparison for the site and process equipment samples. Both the fuel oil blend (FOB) and PS contain a much larger proportion of the lighter materials than do any of the site or process equipment samples. Chemically, these samples resemble the composition of the HD material, or that of the wider-boiling-point-range materials with the lighter ends distilled off.

BaP Concentrations

The process equipment samples represent the types of materials to which coal-liquefaction plant workers may have been exposed whenever process lines were opened for maintenance. Since one of the indicator compounds for assessing carcinogenic potential has often been BaP, each of the process equipment samples was analyzed for BaP concentration. These concentrations, listed in Table 16, were quite variable, ranging from 316 to 5470 ppm in the PAH fractions, and had a mean value of 1558 ppm. From Table 13, the BaP concentration in the PAH fractions of the selected site samples ranged from 300 to 2400 ppm, with a mean BaP concentration in those PAH fractions of 1100 ppm.

The BaP mean values and concentration ranges for all the analyzed PAH fractions isolated from the three sets of pilot-plant decommissioning samples are listed in Table 17, together with the BaP concentration in the PAH fraction of an SRC-II HD sample. While there is wide variability among the samples, the mean BaP concentrations of the pilot-plant decommissioning samples approximates the concentration in the HD material.

GC/MS Analysis of Selected PAH Fractions

GC/MS analysis of the PAH fractions from the selected site samples revealed the presence of three categories of materials: 1) those containing only the characteristic components found in the SRC-II HD product; 2) those that contained the HD characteristic components, but with an increased hydrogenated PAH content; and 3) those that contained the characteristic HD components but were contaminated with high-molecular-weight species derived from

TABLE 15. Concentrations of Selected Compounds in PAH Fractions from SRC-I and SRC-II Product Materials (ppt)

Compound ^a	SRC-II FOB	SRC-I PS	SRC-II HD
Tetralin	1.97 ± 0.05 ^b		
Naphthalene	33.7 ± 0.8	0.578 ± 0.008	
Benzo[b]thiophene	0.550 ± 0.100		
2-Methylnaphthalene	79.5 ± 1.3	24.8 ± 0.6	0.365 ± 0.026
1-Methylnaphthalene	17.1 ± 0.3	4.89 ± 0.10	
Biphenyl	26.0 ± 0.6	18.0 ± 0.4	0.255 ± 0.015
2-Ethylnaphthalene	27.8 ± 0.7		
2,6- or 2,7-Dimethylnaphthalene	44.5 ± 4.1		
1,7-Dimethylnaphthalene	9.74 ± 0.79		
1,6- or 1,3-Dimethylnaphthalene	6.41 ± 0.27	5.95 ± 0.12	0.184 ± 0.024
Acenaphthylene		0.118 ^c	
Acenaphthene	13.7 ± 0.2	17.2 ± 0.4	0.978 ± 0.115
Dibenzofuran	15.9 ± 0.2	37.1 ± 1.3	2.53 ± 0.11
Fluorene	14.4 ± 0.4	41.5 ± 1.2	19.7 ± 0.8
2-Methylfluorene	4.97 ± 0.17		
1-Methylfluorene	9.00 ± 0.31	8.52 ± 0.89	8.63 ± 0.63
Dibenzothiophene	6.93 ± 0.36	15.9 ± 0.4	16.8 ± 0.5
Phenanthrene	39.6 ± 1.9	153 ± 2	117 ± 5
Anthracene	2.46 ± 0.64	4.72 ± 0.20	3.36 ± 0.06
3-Methylphenanthrene	6.36 ± 0.11	21.6 ± 0.1	33.7 ± 1.2
2-Methylphenanthrene	8.04 ± 0.22	23.2 ± 0.5	40.2 ± 1.4
4-H-Cyclopenta[def]-phenanthrene	1.96 ± 0.06	4.21 ± 0.18	2.06 ± 0.61
9- or 4-Methylphenanthrene	2.15 ± 0.05		
1-Methylphenanthrene	2.40 ± 0.06	7.98 ± 0.16	8.67 ± 0.28
Dihydrofluoranthene	1.50 ± 0.03		
Fluoranthene	9.03 ± 0.26	22.0 ± 0.5	13.7 ± 0.7
Acphenanthrylene		0.813 ± 0.466	1.93 ± 0.11
Pyrene	16.5 ± 0.1	24.2 ± 1.2	64.0 ± 3.3
Benzo[a]fluorene	2.24 ± 0.06	5.47 ± 1.11	11.1 ± 1.2
Benzo[b]fluorene or 2- or 4-methylpyrene	7.86 ± 0.16	3.03 ± 0.09	40.9 ± 4.0
1-Methylpyrene	0.929 ± 0.218	2.35 ± 0.12	4.35 ± 0.50
Benzo[b]naphtho[2,1-d]thiophene	0.860 ± 0.930	1.47 ± 0.12	1.96 ± 0.22
Benzo[ghi]fluoranthene		0.733 ± 0.194	2.10 ± 0.17
Benz[a]anthracene	1.33 ± 0.08	2.25 ± 0.11	4.09 ± 0.15

^a Identification based on GC retention time and GC/MS data

^b Represents the average of three determinations at dilutions of 2.50, 5.00 and 1.0 mg/ml

^c One determination only

TABLE 15. (continued)

Compound ^a	SRC-II FOB	SRC-I PS	SRC-II HD
Chrysene ^d	1.90 ± 0.12	3.05 ± 0.14	8.16 ± 0.52
3-Methylchrysene	0.310 ± 0.030	1.23 ± 0.02	2.64 ± 0.33
2-Methylchrysene		0.66 ± 0.05	1.58 ± 0.18
6- or 4-Methylchrysene	1.23 ± 0.03	1.02 ± 0.07	2.91 ± 0.21
1-Methylchrysene	0.339 ^c	0.50 ± 0.20	1.43 ± 0.66
Benzo[j or b]fluoranthene	0.500 ± 0.030	0.289 ± 0.019	2.34 ± 0.21
Benzo[k]fluoranthene	0.130 ± 0.020	0.065 ^c	1.40 ± 0.22
Benzo[e]pyrene	0.590 ± 0.014	0.119 ^c	2.03 ± 0.08
Benzo[a]pyrene	0.560 ± 0.020	0.337 ± 0.047	1.21 ± 0.11
Benzo[ghi]perylene	0.380 ^c	0.378 ± 0.158	1.17 ± 0.34
Perylene			0.628 ± 0.063
Indeno[1,2,3-cd]pyrene		0.103 ^c	0.601 ± 0.047
Dibenz[a,h or a,c]anthracene			0.221 ^c

^a Identification based on GC retention time and GC/MS data

^b Represents the average of three determinations at dilutions of 2.50, 5.00 and 1.0 mg/ml

^c One determination only

^d Co-elutes with triphenylene

rearrangement products of Dowtherm (diphenyl ether), which was used as a heat conductor or thermal transfer material in the pilot plant.

The GC/MS analysis of samples #2515-D09-05 and #2515-015-02 confirmed the presence of only components characteristic of the HD PAH fractions. A typical chromatogram obtained is shown in Figure 2. Table 18 gives the masses and identification of the peaks numbered in Figure 2. PAH and alkylated PAH derivatives from three- to five-ringed parent systems comprised the majority of the components identified. Some neutral sulfur heterocyclic components, i.e., dibenzothiophene and phenanthro[4,5-bcd]thiophene, were also present.

The PAH fraction of sample #2515-007-05 gave similar GC/MS results as samples #2515-009-05 and #2515-015-02, except for the presence of a higher concentration of hydrogenated PAH components. Specifically, components of masses 204, 206, 208, 218, and 256, corresponding to appropriate elution times

TABLE 16. Concentrations of BaP^a in PAH Fractions from Process Equipment Samples. (Astericks denote replicate sample analyses.)

Sample Number	Concentration (ppm)
2515-018-01*	2100 ^b
2515-018-02	1810
2515-018-03 and 03*	981 ^b
2515-018-04	316
2515-018-05 and 05*	1300 ^b
2515-019-01 and 01*	1140 ^b
2515-019-02	5470
2515-019-03	1620
2515-019-04 and 04*	1500 ^b
2515-019-05	1560
2515-020-01	1340
2515-020-02 and 02*	590 ^b
2515-020-03	870
2515-020-04	2200
2515-020-05	1400
2515-022-01	1600
2515-022-02	840
2515-022-03	1500
2515-022-04	1750
2515-022-05 and 05*	1280 ^b
2515-023-01	1420
2515-023-02	1630

^aIdentification based on GC retention time and GC/MS data

^bAverage concentration based on analysis of replicate samples

of dihydrofluoranthene, tetrahydrofluoranthene, hexahydrofluoranthene, C₁-dihydrofluoranthene, and the dihydrobenzofluoranthenes/benzopyrenes, respectively, were detected in significantly higher concentration. This hydrogenated sample may represent a product produced under slightly different coal-liquefaction conditions than the HD material. Three- to five-ring PAH and alkylated PAH derivatives were still the major components identified in the PAH fractions.

TABLE 17. Summary of BaP Contents of PAH Fractions from Decommissioning Samples

Samples	BaP Concentration (ppm)	
	Range	Mean
Pipes and valve scrapings (22 total)	316-5470	1558
Selected scrapings (15 total)	300-2400	1100
Evaporation pond sediments (8 total)	238-1760	976
SRC-II H0		1200

Figure 3 shows a chromatogram of site sample #2515-016-01, PAH fraction, contaminated with the Dowtherm rearrangement products. Peaks numbered in Figure 3 are also identified with their masses in Table 18. This sample represents the worst case of contamination. However, the PAH fractions of samples #2515-009-003, #2515-011-01, and #2515-014-01 were all contaminated with significant quantities of materials at masses 230, 246, 306, 322, and 338. Gas chromatographic peaks of mass 230 gave mass spectral fragmentation patterns characteristic of the terphenyls, as found in the Eight Peak Index of Mass Spectra. Peaks of mass 246 gave mass spectral fragmentation patterns characteristic of the corresponding monophenoxydiphenyl compounds. Peaks of mass 306 gave mass spectral fragmentation patterns characteristic of the quaterphenyls.

High-resolution mass spectrometric analysis of components of masses 306, 322, and 338 assigned elemental compositions of $C_{24}H_{18}$ (a further indication of the quaterphenyls), $C_{24}H_{18}O$, and $C_{24}H_{18}O_2$, respectively. Mass fits were to 1.5 millimass units. These data indicate that the phenoxyterphenyls and the diphenoxydiphenyls were the components present at masses 322 and 338, respectively, although no fragmentation patterns are cataloged in the Eight Peak Index for these compounds.

FIGURE 2. Gas Chromatographic Analysis of the PAH Fraction from Site Sample #2515-015-02. (See text for conditions.)

TABLE 18. Components Identified in the PAH Fractions from Selected Site Samples

Peak Number ^a	Mass	Compound
1	180	C ₁ -Fluorene
2	184	Dibenzothiophene
3	178	Phenanthrene
4	178	Anthracene
5	192	3-Methylphenanthrene
6	192	2-Methylphenanthrene
7	190	4-H-Cyclopenta[def]phenanthrene
8	192	9- or 4-Methylphenanthrene
9	192	1-Methylphenanthrene
10	204	Phenylanthracene
11	212	2-Chloroanthracene, ISTD
12	206	C ₂ -Phenanthrenes
13	204	Dihydrofluoranthene
14	202	Fluoranthene
15	218	C ₁ -Phenylanthracene
16	208	Phenanthro[4,5-bcd]thiophene
17	202	Pyrene
18	230	Terphenyl
19	246	Phenoxydiphenyl
20	230	Terphenyl
21	246	Phenoxydiphenyl
22	216	Benzofluorenes, C ₁ -pyrenes/fluoranthenes
23	232	C ₁ -Benzofluorenes, C ₂ -pyrenes/fluoranthenes
24	234	Benzonaphthothiophene
25	228	Benz[a]anthracene
26	228	Chrysene, triphenylene
27	242	C ₁ -Chrysenes
28	306,322,338	Quaterphenyls, phenoxyterphenyls, diphenoxydiphenyls
29	252	Benzo[j or b]fluoranthene
30	252	Benzo[k]fluoranthene
31	322,338	Phenoxyterphenyl, diphenoxydiphenyl
32	252	Benzo[e]pyrene
33	252	Benzo[a]pyrene
34	306,322,338	Quaterphenyls, phenoxyterphenyls, diphenoxydiphenyls
35	276	Indeno[1,2,3-cd]pyrene
36	278	Dibenz[a,h or a,c]anthracene
37	276	Benzo[ghi]perylene

^aNumbers refer to peaks in Figures 2 and 3

FIGURE 3. Gas Chromatographic Analysis of the PAH Fraction from Site Sample #2515-016-01. (See text for conditions.)

The polyphenyls and polyphenylethers present in the PAH fractions of some of the site samples are likely to be rearrangement products of the Dowtherm (diphenyl ether), which was used in large quantities in the lines of the pilot plant. The neutral behavior of this class of components would allow their elution into the PAH fractions of the contaminated materials. Three- to five-ring PAH and alkylated PAH derivatives characteristic of an SRC-II HD material were the other major components which were analyzed by GC/MS in these samples.

A visual comparison of the chemical composition of the PAH fraction of the HD with those of two site samples is presented in Figure 4. Sample #2515-016-01 is the most highly contaminated with Dowtherm rearrangement products (shown in brackets); sample #2515-015-02 is from the top of the distillation tower in the 04 Area. The contaminants in 016-01 were so concentrated as to overwhelm the other sample constituents. Sample #015-02 resembles the HD PAH fraction, except for the loss of some of the lighter components.

Quantitative Analysis of NPAC in Selected Samples

The concentrations of selected NPAC in 15 site samples are presented in Table 19. In general, the same trends are seen in all of these samples; the principal components of each sample are three-ring systems; carbazole and methylated carbazoles are the most concentrated of these components. Other major constituents include phenanthridine (or benzo[f]quinoline), methylbenzoquinolines, benz[a]acridine, and the azapyrenes. These samples can be compared to samples of the three primary product materials that were produced at the pilot plant (FOB, PS and HD), whose NPAC compositions are listed in Table 20. The relative proportions of sample components most closely resemble the composition of SRC-II HD material. The most concentrated components of the site samples are also the most concentrated components of the HD. Additional constituents, which are rather concentrated in the HD, include the dimethylindoles, benzoquinolines, and acridine. The concentrations of these components in the site samples have been reduced relative to the other components, most likely due to volatilization during weathering.

FIGURE 4. Comparative Gas Chromatographic Analyses of PAH Fractions from SRC-II HD and Site Samples #2515-015-02 and #2515-016-01. Dowtherm rearrangement products are given in brackets. (See text for conditions.)

TABLE 19. Concentrations of Selected Compounds in NPAC Fractions from Selected Site Samples. (Asterisks and R denote replicate sample analyses.)

Compound ^a	Sample Number (Concentration, ppt)							
	2515-008-			2515-009-			2515-011-	
	01R	02* ^b	04	01 ^c	03R	05*	01R	03R
Quinoline					0.30 ± 0.06	0.10		
Indole						0.20		
2-Methylquinoline							0.40	
7-Methylquinoline			0.40		0.40 ± 0.05	0.20	0.40	
2,6- or 2,7-Dimethylquinoline			0.40			0.70	0.70	
1,2-Dimethylindole	0.30 ^d				0.60 ± 0.05			
1,2-Dimethylquinoline						0.50	0.20	
4-Azafluorene					0.10	0.70	0.20	
2,5-Dimethylindole						0.40	0.30	
Benzo[h]quinoline	0.40		0.80		0.70 ± 0.20	1.2	1.0	0.30
Acridine	0.80		0.90		1.55 ± 0.05	1.9	2.3	0.80
Phenanthridine ^e	4.4	0.20	4.6	0.10 ± 0.05	6.35 ± 0.50	11.8	8.6	5.1
Carbazole	22.2	5.4 ± 0.3 ^f	17.4	3.45 ± 0.15	25.3 ± 1.1	38.6	14.8	13.9
2- or 3-Methylbenzo[f]quinoline	1.4		1.7	0.20	2.1 ± 0.20	3.2	2.9	1.5
1-Methylcarbazole		1.0 ± 0.1	1.6	0.90 ± 0.05	5.1 ± 0.30	8.4	5.4	2.9
3-Methylcarbazole	7.5	1.25 ± 0.15	6.1	1.10 ± 0.05	8.6 ± 0.25	11.0	7.1	8.4
2-Methylcarbazole	4.2	0.90 ± 0.10	3.4	0.60 ± 0.05	4.6 ± 0.30	6.3	3.2	3.8
4-Methylcarbazole	1.5	1.6 ± 0.1	1.9	1.5	3.0 ± 0.60	4.4	5.6	2.7
1- or 2-Azafluoranthene	0.50	1.0 ± 0.1	0.60	0.20	0.80 ± 0.20		1.0	0.70
7-Azafluoranthene					0.25	0.60	0.20	0.05

^aIdentification based on GC retention time^bSample contained a contaminant with a concentration of about 360 ppt^cSample contained a contaminant with a concentration of about 240 ppt^dRepresents one determination at 5.0 mg/ml^eCo-elutes with benzo[f]quinoline^fAverage of two determinations at 5.0 mg/ml

TABLE 19. (continued)

Compound ^a	Sample Number (Concentration, ppt)						
	2515-008-			2515-009-			2515-011-
	01R	02* ^b	04	01 ^c	03R	05*	01R 03R
1- or 4-Azapyrene	2.2	0.10	1.5	0.15 ± 0.10	2.0 ± 0.10	1.2	1.6 3.9
2-Azapyrene	1.6	1.35 ± 0.35	1.7	1.5 ± 0.4	1.65 ± 0.30	1.8	2.2 1.6
9-Phenylcarbazole					0.45	0.60	0.50
Benz[c]acridine					0.15		0.10
Benz[a]acridine		2.05 ± 0.05	0.40	0.95 ± 0.15	3.2 ± 0.2	0.40	2.6 3.4
1-Azabenz[a]anthracene		0.40	1.1	0.60	0.20	0.30	0.50
Benzo[a]carbazole	2.5	0.50	1.6	0.30	2.7 ± 0.1	2.5	2.45 4.3
1-Azachrysene		0.25 ± 0.20		0.15			0.70
47 Benzo[b]carbazole	1.9	1.9 ± 0.10	2.0	2.1 ± 0.15	1.9 ± 0.05	1.1	1.5 3.3
Benzo[c]carbazole		0.70			0.50 ± 0.10		0.30 0.60
10-Azabenz[a]pyrene ^d							
Dibenzo[a,i]carbazole							
Dibenzo[c,g or a,g]carbazole							

^aIdentification based on GC retention time

^bSample contained a contaminant with a concentration of about 360 ppt

^cSample contained a contaminant with a concentration of about 240 ppt

^dCo-elutes with dibenz[a,j]acridine

TABLE 19. (continued)

Compound ^a	Sample Number (Concentration, ppt)						
	2515-012-		2515-015-		2515-016-	2515-017	2515-021
	03 ^b	05R	02	03*	01*	03*	05*
Quinoline							
Indole							
2-Methylquinoline					0.40	0.20	
7-Methylquinoline					0.60	0.20	0.10
2,6- or 2,7-Dimethylquinoline		0.40			0.60	1.1	0.50
1,2-Dimethylindole						0.40	
1,2-Dimethylquinoline					0.20	0.40	
4-Azafluorene		0.050			0.10	0.50	0.50
2,5-Dimethylindole					0.30	0.40	0.30
48 Benzo[h]quinoline	0.50	1.1	0.30	1.3	0.90	1.2	0.80
Acridine	0.10	1.1	1.3	0.40	1.6	2.4	1.0
Phenanthridine ^c	1.1	4.5	7.6	5.3	7.8	8.2	6.8
Carbazole	5.6	22.7	31.7	25.6	20.2	4.2	18.0
2- or 3-Methylbenzo[f]quinoline	0.40	1.9	2.5	1.9	2.3	3.4	2.3
1-Methylcarbazole	1.3	3.5	5.5	5.4	5.3	8.5	4.8
3-Methylcarbazole	2.7	7.9	8.9	6.6	8.8	7.9	7.6
2-Methylcarbazole	1.4	4.4	5.4	4.0	4.2	2.6	3.7
4-Methylcarbazole	1.0	3.0	3.7	3.3	11.3	7.8	2.5
1- or 2-Azafluoranthene	0.30	0.40	1.0	1.1	0.90	1.4	1.3
7-Azafluoranthene			0.20	0.30	0.30	1.0	0.25
1- or 4-Azapyrene	1.0	2.1	3.0	2.2	2.5	2.5	2.3
2-Azapyrene	1.2	1.9	2.9	2.0	2.4	3.6	1.9
9-Phenylcarbazole			1.2	0.20		1.0	0.20
Benz[c]acridine			0.30	2.1		0.10	

^aIdentification based on GC retention time^bSample contained a contaminant with a concentration of about 200 ppt^cCo-elutes with benzo[f]quinoline

TABLE 19. (continued)

Compound ^a	Sample Number (Concentration, ppt)						
	2515-012-		2515-015-		2515-016-	2515-017	2515-021
	03 ^b	05R	02	03*	01*	03*	05*
Benz[a]acridine	0.50	0.10	3.4	7.0	3.2	1.0	4.4
1-Azabenz[a]anthracene		3.3		0.90		0.30	20.6
Benzo[a]carbazole		2.4	5.3	3.0	3.0	3.0	3.4
1-Azachrysene				1.2	0.30		0.40
Benzo[b]carbazole		2.3	3.2	4.6	2.2	2.3	2.2
Benzo[c]carbazole			0.20	1.5	0.50		1.0
10-Azabenz[a]pyrene					0.50		
Dibenzo[a,i]carbazole ^c				0.40	0.50		
Dibenzo[c,g or a,g]carbazole				0.50			

^aIdentification based on GC retention time

^bSample contained a contaminant with a concentration of about 200,000 ppm

^cCo-elutes with dibenz[a,j]acridine

TABLE 20. Concentrations of Selected Compounds in the NPAC Fractions from SRC-I and -II Product Materials (ppt)

Compound ^a	SRC-II FOB	SRC-I PS	SRC-II HD
Aniline	2.83 ± 0.62 ^b		
Methylaniline	12.7 ± 3.0		
Methylaniline	5.30 ± 1.22		
Tetrahydroquinoline	6.48 ± 2.12		
Quinoline	10.6 ± 2.3	2.45 ± 0.02	0.066 ^c
Isoquinoline	1.40 ± 0.28	0.418 ± 0.030	
Indole	16.7 ± 3.2	4.16 ± 0.05	0.084 ^c
2-Methylquinoline	14.8 ± 2.9	6.17 ± 0.32	0.256 ± 0.048
8-Methylquinoline	1.99 ± 0.25		
7-Methylquinoline	13.5 ± 3.3		
3-Methylquinoline	7.12 ± 3.19	4.29 ± 0.11	0.207 ± 0.053
4-Methylquinoline		1.18 ± 0.83	0.104 ± 0.016
3-Methylindole	9.47 ± 2.4		
2-Methylindole	4.87 ± 0.64		
2,6- or 2,7-Dimethylquinoline	6.88 ± 2.41	6.38 ± 1.83	0.870 ± 0.274
2,5-Dimethylindole	4.20 ± 0.89	4.13 ± 1.95	0.149 ± 0.002
2,3-Dimethylindole	3.56 ± 0.62	1.27 ± 0.05	1.80 ± 0.20
4-Azafluorene		0.946 ± 0.205	0.748 ± 0.210
Benzo[h]quinoline	2.20 ± 0.03	5.52 ± 0.67	9.96 ± 1.03
Acridine	0.899 ± 0.076	3.94 ± 0.53	5.66 ^c
Phenanthridine or benzo[f]-quinoline	3.28 ± 0.13	7.84 ± 0.78	20.8 ± 1.1
Carbazole	16.0 ± 0.6	32.0 ± 2.9	90.3 ± 10.6
2- or 3-Methylbenzo[f]quinoline	1.13 ± 0.17	2.78 ± 0.91	6.81 ± 0.70
1-Methylacridine	1.47 ± 0.18		
1-Methylcarbazole ^d	2.21 ± 0.12	6.59 ± 0.25	13.2 ± 0.3
3-Methylcarbazole	5.15 ± 0.22	9.60 ± 0.45	31.6 ± 3.3
2-Methylcarbazole	3.60 ± 0.14	6.12 ± 0.56	15.8 ± 1.9
4-Methylcarbazole	1.21 ± 0.08	4.03 ± 0.48	8.42 ± 0.37
1- or 2-Azafluoranthene	1.35 ± 0.67	1.25 ± 0.07	1.75 ± 0.78
7-Azafluoranthene	1.53 ± 0.98	0.750 ^c	2.06 ± 0.33
1- or 4-Azaperyrene	3.68 ± 1.71	1.76 ± 0.81	14.0 ± 3.9
Benz[c]acridine		1.31 ± 0.01	1.66 ± 0.22
Benz[a]acridine		1.49 ± 0.28	0.86 ± 0.23
Benzo[a]carbazole	2.79 ± 1.07	2.37 ± 0.09	7.60 ± 0.60
1-Azachrysene		0.16 ± 0.01	0.527 ± 0.198
Benzo[b]carbazole	1.57 ± 0.59	1.63 ± 0.05	3.89 ± 0.42

^aIdentification based on GC retention time and GC/MS data

^bRepresents the average of three determinations at dilutions of 2.50, 5.00 and 10.0 mg/ml

^cOne determination only

^dCo-elutes with 2-methylacridine

TABLE 20. (continued)

Compound ^a	SRC-II FOB	SRC-I PS	SRC-II HD
Benzo[c]carbazole or 2-Azachrysene	2.65 ± 1.25 ^b	1.81 ± 0.07	6.73 ± 0.16
10-Azabenz[a]pyrene		0.112 ± 0.019	0.620 ± 0.209
Dibenzo[a,i]carbazole or [a,j]acridine	0.37 ^c		0.352 ± 0.120
Dibenzo[c,g or a,g]carbazole	1.04 ^c		0.561 ± 0.333

^aIdentification based on GC retention time and GC/MS data

^bRepresents the average of three determinations at dilutions of 2.50, 5.00 and 10.0 mg/ml

^cOne determination only

Quantitative Analysis of Amino-PAH in Selected Samples

A few site samples which were analyzed quantitatively for NPAC components were further fractionated, chemically derivatized, and analyzed for amino-PAH concentrations. The data from these analyses are listed in Table 21, where the amino-PAH concentrations are compared to those in SRC-II HD material. While other data previously discussed have shown similar relative concentrations between components of the site samples and the HD material, the amino-PAH data do not show this similarity. The amine concentrations in the five site samples which were examined were greatly reduced from the corresponding concentrations in the HD. (The 14,000-ppm concentration of 6-aminochrysene [6-AC] in sample #2515-012-03 is believed to be a large contaminant that carried into this fraction.) These reductions in amino-PAH concentrations are consistent with the results of laboratory studies by Kalkwarf et. al. (1984) and Wright and Weimer (1984). These investigations demonstrated that exposure of coal liquids to light and/or air reduced the amino-PAH content of the liquids to near zero. This reduction in amino-PAH content is shown graphically in Figure 5. The top portion of this figure is the GC electron capture detector response for the amino-PAH-enriched fraction of a sample of SRC-II FOB. The bottom portion of the figure is the GC response for the same PFPA-deriva-

TABLE 21. Concentrations of Selected Compounds in the Amino-PAH-Enriched Fractions from Selected Site Samples and Product Materials. (Asterisks and R denote replicate sample analyses.)

Compound ^b	Sample Number (Average Concentration, ppm) ^a					SRC-II HO
	2515-008-01R	2515-008-02** ^c	2515-009-01 ^c	2515-009-03R	2515-012-03 ^c	
5-Aminoindan						150
1-Aminonaphthalene	37.1					3,890
2-Aminobiphenyl	264 ± 26			13.0 ± 2.2		1,475
2-Aminonaphthalene	31.1 ± 6.9			11.2 ± 0.2	6.89 ± 9.62	17,100
3-Methyl-2-amino-naphthalene	51.1 ± 10.6			10.1		
4-Aminobiphenyl	81.2 ± 13.7	23.9 ± 7.3	26.0 ± 7.2	23.7 ± 2.3	14.3	3,160
4-Aminofluorene	93.3 ± 35.3			18.5 ± 8.0		
2-Aminofluorene	115 ± 38	235 ± 52	92.7 ± 6.4	152 ± 2	40.3 ± 23.4	57,990
1- and 9-Aminophenanthrene ^d	210 ± 102	188 ± 79	646 ± 117	245 ± 62	196 ± 48	17,345
3-Aminophenanthrene	183 ± 59	73.2 ± 37.4	60.4 ± 13.0	78.8 ± 26.5	51.4 ± 19.6	
2-Aminoanthracene	153 ± 91	44.7 ± 14.3	82.6 ± 11.4	66.9 ± 25.3		
2-Aminophenanthrene						19,750
3-Aminofluoranthene	25.8		111			2,500
1-Aminopyrene	616 ± 210	194 ± 18	143 ± 18	108	87.9 ± 41.9	4,715
2-Aminopyrene	171 ± 34	1440 ± 95	351 ± 115	292 ± 80	250 ± 56	
8-Aminofluoranthene	538 ± 170	775 ± 173		808 ± 177	14,000 ± 150	
6-Aminochrysene		605 ± 245	406 ± 117	476 ± 37	198 ± 140	
3-Aminochrysene	300 ± 140	339 ± 129	135 ± 16	290 ± 37	186	
7-Aminobenzo[a]-pyrene		107 ± 12	199 ± 30	474 ± 112		

^aIdentifications based on GC retention times from responses of PFPA derivatives to electron capture detection

^bBased on three determinations at 10.0, 5.00 and 2.50 mg/ml

^cVery large contaminant peak between 8-aminofluoranthene and 6-aminochrysene

^dCo-elutes with 1-aminoanthracene

FIGURE 5. Gas Chromatographic Analysis of Derivatized Amino-PAH-Enriched Fraction of SRC-II FOB. (See text for conditions.)

tized fraction of an FOB sample after storage under conditions of accelerated aging. The reduction in detector response is apparent. From the limited data available for the site samples, this same destruction of amino-PAH appears to have occurred during the natural weathering of the coal liquids.

Simulated Distillation of Selected Samples

Three of the site samples that were examined for their biological activity were also subjected to simulated distillation analysis by GC. Previously, simulated distillation analysis of all Ft. Lewis pilot-plant product materials had been performed periodically as a measure of sample stability. The distillation curves (percent off versus temperature) of the site samples are compared to that of the SRC-II HD product material in Figure 6. The distillation curves show graphically that these site samples have the same upper-boiling-point limit as does the HD and that they have lost some of the lower-boiling components. The result of this loss is the slight shifting of the curves to higher temperatures for a given percent-off value. Nevertheless, the distillation profiles of these environmental samples closely resemble the profile of the HD material.

GC/MS Analysis of Selected HPAH Fractions

Results from the GC/MS analysis of the five selected HPAH fractions of the site samples can be categorized into two sets. The first set consists of those samples that contain the compounds characteristic of an HPAH fraction of the SRC-II HD, with some unknown and/or nitrogen-containing compound contamination. The second set consists of those samples that contain as yet unidentified oxygen-containing polar components.

The HPAH fractions from samples #2515-007-05 and #2515-009-05 were composed of the characteristic HPAH fraction constituents of SRC-II HD product materials, as shown in Table 22. Sample #2515-007-05 also had major contamination from species of masses 179, 167, 181, 193, 195, 203, 217 and 231. These masses were identified as the NPAC of the benzoquinolines, carbazole, C₁-carbazoles, C₁-benzoquinolines, C₂-carbazoles, azapyrenes/fluoranthenes, C₁-azapyrenes/fluoranthenes, benzocarbazoles and C₁-benzocarbazoles, respectively.

FIGURE 6. Simulated Distillation of Selected Site Samples

TABLE 22. Characteristic Components Identified in the HPAH Fractions from Site Samples #2515-007-05 and #2515-009-05

Mass ^a	Compound
94	Phenol
108	C ₁ -Phenol
122	C ₂ -Phenols
136	C ₃ -Phenols
134	Indanols
150	C ₄ -Phenols
148	C ₁ -Indanols
164	C ₅ -Phenols
170	Hydroxybiphenyls/acenaphthenes
162	C ₂ -Indanols
178	C ₆ -Phenols
184	C ₁ -Hydroxybiphenyls/acenaphthenes
192	C ₇ -Phenols
198	C ₂ -Hydroxybiphenyls/acenaphthenes
182	Hydroxyfluorenes
196	C ₁ -Hydroxyfluorenes
220	Naphthylphenol
234	C ₁ -Naphthylphenol

^aGiven in order of chromatographic elution

The apparent large HPAH content of this sample was probably due to the presence of these NPAC species, which should have eluted earlier in the alumina column chromatographic step. Other unknown constituents found in the HPAH fraction of sample #2515-007-05 gave a molecular ion peak of mass 71 with mass 43 as the second most abundant. At least 10 separate peaks from the GC/MS analysis gave these two ions as fragments. Mass 71 is believed to represent a fragment from a higher-molecular-weight compound, for which chemical ionization (CI) MS would be needed for further identification.

As mentioned above, the components listed in Table 22 were also identified in sample #2515-009-03. Carbazole (mass 167) contamination was negligible in this sample fraction. The major component in this fraction gave a molecular ion peak of mass 154 when analyzed using splitless injection. The mass spectrum was characteristic of biphenyl. When analyzed using on-column

injection, the peak of mass 154 was no longer present. It is believed that this major component was a rearrangement product of some species (perhaps from Dowtherm) which is formed under the harsh conditions in the injection port with the splitless injection technique. Unfortunately, when analyzed with on-column injection, no major component was identified that could account for the rearrangement product formed in the injection port. Either the component was too polar or too nonvolatile to be chromatographed under the conditions employed.

GC/MS analyses of the HPAH fractions of samples #2515-009-03, #2515-011-01 and #2515-014-01 gave similar results. The components expected (and listed in Table 22) were present only in trace amounts or were not present at all in these samples. Contamination from carbazole (m/e 167) and C₁-carbazoles (m/e 181) was low. The major components (constituting approximately 10% of each sample) gave fragment ion peaks of masses 71 or 44 in the highest abundance; secondary fragment ion peaks of masses 43 and 87 were noted with the 71 mass; secondary fragment ion peaks of masses 57 and 71 were noted with the 44 mass. High-resolution MS analysis assigned elemental compositions of C₂H₃O or C₃H₇, C₄H₇O, and C₄H₇O₂ for the masses of 43, 71 and 87, respectively. Although the spectra from the Eight Peak Index of Mass Spectra were not identical, the spectra for some methyl or methylhydroxy-substituted tetrahydrofurans and esters with at least one C₄ side chain were similar to those unknowns in the samples analyzed that gave fragment ions of 71, 43, and 87. The components with the largest fragment ion at m/e 44 had spectra similar to some carboxylic acids. CI MS may give more insight into the exact structures of the components found in these fractions, since it is believed that no molecular ion peaks were given under the electron impact mode of operation. Many of the components found in high concentration in these three fractions gave the same spectra and elution times as the contaminants found in low concentrations in the HPAH fraction of sample #2515-007-05.

Microbial Mutagenicity

The three site samples selected for bioassay studies are listed in Table 23; both microbial mutagenicity and I/P investigations were performed. These samples were chosen for several reasons. They all had relatively high

TABLE 23. Identification of Samples Used for Mutagenicity and I/P Investigations

Sample Number ^a	Description
2515-09-03	Scrapings from conditioning drum inside building (no direct exposure to rain or sunlight)--03 Area
2515-11-01	Scrapings from beneath sampling valve, ground level (exposed to sunlight and rain)--03 Area
2515-16-01	Drippings from valve below vacuum flash drum, ground level (minimal direct exposure to rain and sunlight)--04 Area

^aSee Table 2 for description

concentrations of four-ring-and-larger PAH components, based on the initial semiquantitative analysis of the PAH fractions. Subsequent analyses also showed that samples #2515-009-03 and #2515-011-01 contained larger than average proportions of NPAC and HPAH fractions. Sample #2515-016-01 contained a very large PAH fraction (later demonstrated to be due largely to contamination by Dowtherm, as described above).

The data from the microbial mutagenicity analysis of the dissolved portions and subsequent chemical class fractions from these samples are given in Table 24, along with the corresponding data for SRC-II HD. The site samples were, essentially, nonmutagenic when compared to the HD material. Residual low levels of microbial mutagenicity were detected only in the HPAH fractions of the site samples tested. The microbial mutagenicity of the NPAC fractions from the environmentally weathered site samples was in direct contrast to that of the SRC-II HD; no activity was detected in the site samples, whereas the majority of the mutagenicity detected in the HD was present in the NPAC fraction. These data are consistent with the fact that the amino-PAH content of the site samples was quite low. The amino-PAH have been previously identified as the most mutagenic compounds found in coal-derived materials (Wilson et al., 1980; Guerin et al., 1980). The data are also in agreement with that of

TABLE 24. Mutagenicity of Selected Site Samples

Sample	Revertants/ μ g
2515-09-03 ^a	1.1
AH	0
PAH	0
NPAC	0
HPAH	1.4
2515-11-01 ^a	0
AH	0
PAH	0
NPAC	0
HPAH	2.1
2515-16-01 ^a	
AH	0
PAH	0
NPAC	0
HPAH	0.8
SRC-II HD	
AH	0
PAH	0
NPAC	175
HPAH	0.5

^aRepresents solvent-soluble portions, as previously described

Kalkwarf et al. (1984), Wright and Weimer (1984) and Wright et al. (1985), who demonstrated that exposure of coal liquids to air and/or sunlight eliminated or greatly reduced the microbial mutagenicity of the materials. The data from these workers, along with the data for these three samples, would suggest that any of the site samples that had been exposed to environmental conditions would likely have low mutagenic activity as a result of the decreased amino-PAH content.

Initiation/Promotion (I/P)

The I/P investigations of the samples listed in Table 23 demonstrated that all three of these samples were biologically active. Figure 7 presents the results of this study both in terms of cumulative number of total tumors per test group (upper figure) and the cumulative percent incidence of tumor formation (lower figure). The total number of tumors produced ranged from 77 to 97 per test group; the percent incidence of tumor formation was 90 to 100%. A comparison of these levels of activity with the results of I/P studies performed with two product materials and several boiling-point cuts of SRC materials is given in Table 25. In terms of both percent incidence of tumors and total number of tumors induced, these three environmentally weathered site samples resembled the SRC-II HD product. These data, together with the data just discussed above, suggest that, while the microbial mutagenicity of the site samples has been eliminated by the environmental weathering process, the mixture of compounds responsible for the tumorigenic response of the coal liquids has been relatively unaffected. The hazards of exposure to weathered coal-liquid materials are therefore likely to be the same as those from exposure to the original coal liquid.

SEDIMENT SAMPLES

Quantitative Analysis of PAH

The results of quantitating selected PAH in the sediments from the evaporation pond for treated wastewater are presented in Table 26. These data are grouped in pairs, representing the upper and lower portions of the sediment cores, with the data for the upper cores presented first in each pair. Three of the samples were lost during processing, so data are missing for some of the samples that were described in Table 1. For the four sets of samples that represent entire sediment cores, the PAH concentrations in the upper core segment are significantly greater than those in the lower segments. The lower segments, #2222-081-09 and #2222-081-11, had levels of PAH comparable to those of sample #2222-081-02, which is a topsoil and represents background concentrations for soil near the pilot plant. Lower segments #2222-081-07 and #2222-081-08 had higher-than-background PAH concentrations and showed that the

FIGURE 7. I/P Results for Selected Site Samples. Top: Cumulative number of total tumors per test group, adjusted to 30 animals per group. Bottom: Cumulative percent incidence of tumor formation.

TABLE 25. I/P Results for Selected Site Samples and Product Materials

Sample	Percent Incidence of Tumors	Total Number of Tumors
2515-11-01	100	77
2515-16-01	90	107
2515-09-03	97	97
SRC-II HD	90	100
850°F+	95	205
800-850°F	63	32
750-800°F	33	13
700-750°F	35	17
SRC-I PS	82	62
800-850°F	94	93
750-800°F	76	38
700-750°F	41	11

coal-liquid contamination had penetrated deeply into the sediments (at least 22 and 20 inches of penetration, respectively). The average concentration of BaP in the PAH fraction of the sediment samples (see Table 17) was 976 ppm. This concentration is comparable to the average concentrations found in the environmental scrapings and in the pipes and valve scrapings, as well as approximating that found in the SRC-II HD material. Because of the generally high PAH concentrations found in these sediments, the State of Washington Department of Ecology required that these sediments be removed from the site as part of the pilot-plant decommissioning process.

Quantitative Analysis of Amino-PAH

Analyses of the NPAC fractions from the sediments showed carbazole to be the only component quantifiable under the standard operating conditions employed. Minimum detectable limits were approximately 50 ppm. Since it was desirable to evaluate whether amino-PAH were present in these sediment samples, additional fractionation and analysis of selected NPAC fractions were performed on three samples. The data from these analyses are listed in Ta-

ble 27. The amino-PAH concentrations in these sediment samples are markedly lower than the corresponding concentrations in the SRC-II HD material (data given in Table 21) but higher than in the several environmental site samples that were analyzed. The sediments, because of their dark, anoxic environment, appeared to preserve the amino-PAH for longer than might be predicted based on the previously cited laboratory investigations (Kalkwarf et al., 1984; Wright and Weimer, 1984).

TABLE 26. Concentrations of Selected Compounds in PAH Fractions from Sediment Samples^a

Compound ^b	Sample Number 2222-081- (Concentration, ppt)								
	04 ^c	07 ^c	03 ^d	08 ^e	05 ^c	09 ^f	06 ^c	11 ^g	02 ^c
Biphenyl	0.148								
Dibenzofuran	0.357 ± 0.006		0.136 ± 0.012				0.117 ± 0.034		
Fluorene	0.628 ± 0.013		0.405 ± 0.101		0.143 ± 0.013		0.074		
1-Methylfluorene	1.89 ± 0.22		1.02 ± 0.388	0.172	1.52 ± 0.01		0.608 ± 0.040		0.262 ± 0.036
Dibenzothiophene	1.97 ± 0.32		0.861 ± 0.293		1.34 ± 0.11		0.391 ± 0.226		0.171 ± 0.110
Phenanthrene	9.84 ± 0.70	1.60 ± 0.07	6.16 ± 2.06	2.05 ± 0.23	2.98 ± 0.24	0.217	1.98 ± 0.37	0.477 ± 0.086	0.267 ± 0.059
3-Methylphenanthrene	4.08 ± 0.15	0.382 ± 0.048	3.21 ± 0.12	0.896 ± 0.057	2.62 ± 0.18		1.71 ± 0.13	0.119	0.291 ± 0.059
2-Methylphenanthrene	5.39 ± 0.01	0.570 ± 0.025	4.08 ± 0.83	1.22 ± 0.04	3.31 ± 0.29		2.12 ± 0.19	0.345	
4-H-Cyclopenta[def]-phenanthrene	1.62 ± 0.02		1.19 ± 0.24	0.275 ± 0.124	3.73 ± 0.21		0.844 ± 0.369	0.037	
1-Methylphenanthrene	1.93 ± 0.06	0.189 ± 0.150	1.58 ± 0.09	0.351 ± 0.121	1.12 ± 0.03		0.908 ± 0.103		
Fluoranthene	14.0 ± 0.9	2.09 ± 0.04	9.09 ± 0.44	4.35 ± 0.15	17.4 ± 0.4	0.500	9.47 ± 0.40	1.17 ± 0.06	0.568 ± 0.014
Pyrene	19.0 ± 1.2	2.46 ± 0.13	14.4 ± 0.4	6.07 ± 0.12	24.1 ± 1.89	0.608	13.5 ± 1.04	1.69 ± 0.19	0.685 ± 0.038
Benzo[a]fluorene ^h	3.54 ± 1.23	0.378 ± 0.178	2.48 ± 0.57	1.32 ± 0.12	5.83 ± 0.71	0.174	6.12 ± 0.38	0.481 ± 0.106	0.744 ± 0.150
Benzo[b]fluorene ^h	7.08 ± 0.97	0.586 ± 0.021	4.43 ± 0.37	2.14 ± 0.06	6.78 ± 0.63	0.146	5.92 ± 0.12	0.461 ± 0.056	0.300 ± 0.013
1-Methylpyrene	2.02 ± 0.24	0.193 ± 0.129	1.92 ± 0.77	0.475 ± 0.004	2.05 ± 0.44		2.02 ± 0.08	0.351 ± 0.014	
Benz[a]anthracene	2.38 ± 0.01	0.281 ± 0.021	1.75 ± 0.21	0.781 ± 0.038	2.63 ± 0.57		2.35 ± 0.46	0.526 ± 0.166	0.149 ± 0.006
Chrysene	3.91 ± 0.02	0.748 ± 0.018	2.58 ± 0.45	1.77 ± 0.17	5.68 ± 0.94		5.34 ± 0.69	0.564	0.698 ± 0.054
3-Methylchrysene	0.947 ± 0.151	0.102	0.455 ± 0.086	0.313	0.970 ± 0.291		0.775 ± 0.204		

^aSamples 01, 10 and 12 were unavailable for analysis^bIdentification based on GC retention time and GC/MS data^cBased on three determinations at 10.0, 5.00 and 2.50 mg/ml^dBased on two determinations at 10.0 and 5.00 mg/ml^eBased on two determinations at 10.0 and 2.50 mg/ml^fBased on one determination at 10.0 mg/ml^gBased on two determinations at 5.00 and 2.5 mg/ml^hCo-elutes with 2- or 4-methylpyreneⁱCo-elutes with triphenylene

TABLE 26. (continued)

Compound ^b	Sample Number 2222-081- (Concentration, ppt)								
	04 ^c	07 ^c	03 ^d	08 ^e	05 ^c	09 ^f	06 ^c	11 ^g	02 ^c
2-Methylchrysene	0.350		0.122		0.351 ± 0.038		0.792 ± 0.163		
6- or 4-Methylchrysene	1.29 ± 0.31	0.196	1.11 ± 0.11	0.676 ± 0.139	1.71 ± 0.37		2.47 ± 0.46	0.903	0.614 ± 0.267
1-Methylchrysene	0.633 ± 0.168		0.345 ± 0.089	0.215	0.796 ± 0.264		0.744 ± 0.141		
Benzo[j] or b[fluoranthene	1.86 ± 0.32	0.479 ± 0.173	1.40 ± 0.24	0.814 ± 0.067	3.27 ± 0.07		3.18 ± 0.631	0.254	0.607 ± 0.234
Benzo[k]fluoranthene				0.217	0.717		0.568		
Benzo[e]pyrene	1.45 ± 0.062	0.421 ± 0.037	1.38 ± 0.33	0.953 ± 0.144	2.20 ± 0.21		2.77 ± 0.53	0.562 ± 0.052	1.00 ± 0.16
Benzo[a]pyrene	0.930 ± 0.049	0.238 ± 0.021	0.768 ± 0.163	0.511 ± 0.073	1.27 ± 0.03		1.69 ± 0.25		0.641 ± 0.113
Perylene	0.177 ± 0.026	0.354 ± 0.071	0.354 ± 0.302	0.254	0.665 ± 0.245		0.856 ± 0.315		0.193 ± 0.014
Indeno[1,2,3-cd]-pyrene	0.553 ± 0.033	0.277 ± 0.052	0.857 ± 0.115	0.608 ± 0.086	0.889 ± 0.160		1.71 ± 0.46	0.665 ± 0.116	1.140 ± 0.13
Dibenz[a,h or a,c]-anthracene					0.268 ± 0.092		0.311 ± 0.251		
Benzo[ghi]perylene	0.908 ± 0.15/	0.327 ± 0.040	1.68 ± 0.14	0.893 ± 0.134	0.982 ± 0.347		2.34 ± 0.38	0.795 ± 0.047	1.740 ± 0.22

^aSamples 01, 10 and 12 were unavailable for analysis^bIdentification based on GC retention time and GC/MS data^cBased on three determinations at 10.0, 5.00 and 2.50 mg/ml^dBased on two determinations at 10.0 and 5.00 mg/ml^eBased on two determinations at 10.0 and 2.50 mg/ml^fBased on one determination at 10.0 mg/ml^gBased on two determinations at 5.00 and 2.5 mg/ml^hCo-elutes with 2- or 4-methylpyreneⁱCo-elutes with triphenylene

TABLE 27. Concentrations of Selected Compounds in the Amino-PAH-Enriched Fractions from Selected Sediment Samples

Compound ^b	Sample Number, 2222-081- (Average Concentration, ppm) ^a		
	05	06	10
1-Aminonaphthalene	--	--	33 ± 5
2-Aminofluorene	2540 ± 760	1550 ± 100	1840 ± 70
1- or 9-Aminophenanthrene ^c	--	--	87 ± 11
2- or 3-Aminophenanthrene	659 ± 188	609 ± 79	430 ± 19
3-Aminofluoranthene	--	--	1000 ± 120
2-Aminopyrene	877 ± 264	557 ± 151	750 ± 123
6-Aminochrysene	223 ± 53	--	128 ± 49
3-Aminochrysene	559 ± 212	743 ± 375	582 ± 378

^aBased on three determinations, at 10.0, 5.00 and 2.50 mg/ml

^bIdentifications based on GC retention times from responses of PFPA derivatives to electron capture detection

^cCo-elutes with 1-aminoanthracene

CONCLUSIONS

The following conclusions may be drawn from the results of the investigations of the samples collected during the decommissioning of the Ft. Lewis SRC pilot plant:

1. The environmental residues of coal liquids in the site and process equipment samples closely resembled SRC-II HD material in overall chemical composition.
2. The average BaP concentrations in 8 (of 9 analyzed) evaporation pond sediments, 15 (of 16 analyzed) selected site samples, and 22 (of 22 analyzed) process equipment samples all approximate the BaP concentrations in HD material.
3. An important difference in chemical composition between the HD material and the site samples and process equipment samples was the low level of amino-PAH found in the latter compared to the relatively higher concentration found in the HD.
4. The environmental transformations, as measured by chemical analysis of these samples, agree with those predicted by previous laboratory investigations.
5. GC/MS analysis of selected samples has shown that the site samples contain as-yet-unidentified polar (likely to be oxygen-containing) components not present in SRC-II HD.
6. The level of residual microbial mutagenicity found in three selected site samples was significantly lower than that of the HD material because of the low amino-PAH content of the site samples.
7. The biological response of three selected site samples in the I/P mouse-skin tumor assay was comparable to that found for SRC-II HD.

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Washington, DC 20545

M. J. Eaman
Concord Scientific Corporation
641 Montreal Road, #200
Ottawa, Ontario, K1K-0T4
CANADA

H. Enoch
Kentucky Department of Energy
P. O. Box 11888
Lexington, KY 40578

J. L. Epler
Oak Ridge National Laboratory
P. O. Box X
Oak Ridge, TN 37830

J. P. Fillo
Environmental Research and
Technology, Inc.
601 Grant Street
Porter Building, 10th Floor
Pittsburgh, PA 15219

S. Foster
Energy and Environmental Analysis,
Inc.
1111 North 19th Street
Arlington, VA 22209

L. Fradkin
Argonne National Laboratory
Building 12
Argonne, IL 60439

M. R. J. Fry
Oak Ridge National Laboratory
P. O. Box X
Oak Ridge, TN 37830

R. Fry
FE-40, GTN
U.S. Department of Energy
Washington, DC 20545

K. Frye
FE-40, GTN
U.S. Department of Energy
Washington, DC 20545

A. A. Galli
U.S. Environmental Protection Agency
401 M Street, SW
Washington, DC 20460

M. Gatti
Ente Nazionale per l'Energia
Elettrica
G. B. Martini 3
00100 Rome
ITALY

C. W. Gehrs
Oak Ridge National Laboratory
P. O. Box X
Oak Ridge, TN 37830

H. Gerstenkorn
Ruhrkohle Oel und Gas GMBH
Gleiwitzer Platz 3
4250 Bottrop
FEDERAL REPUBLIC OF GERMANY

J. M. Giddings
Oak Ridge National Laboratory
P. O. Box X
Oak Ridge, TN 37830

G. F. Goethel
VEBA OEL AG
Postfach 45
4660 Gelsenkirchen-Buer
FEDERAL REPUBLIC OF GERMANY

L. Goldberg
Chemical Industrial Institute of
Toxicology
2109 Nancy Ann Drive
Raleigh, NC 27607

G. Goldstein
ER-74, GTN
U.S. Department of Energy
Washington, DC 20545

S. Gottlieb
Synthetic Fuels Corporation
2121 K Street, NW
Washington, DC 20586

J. R. Gough
Catalytic, Inc.
P. O. Box 239
Wilsonville, AL 35186

J. Gray
Ashland Synthetic Fuels, Inc.
P. O. Box 391
Ashland, KY 41101

M. D. Gray
NCB (Coal Products), Ltd.
Coal House, Lyon Road
Harrow, HA1 2EX
ENGLAND

M. Green
The Lummus Company
1515 Broad Street
Bloomfield, NJ 07003

R. A. Griesemer
Oak Ridge National Laboratory
P. O. Box X
Oak Ridge, TN 37830

M. R. Guerin
Oak Ridge National Laboratory
P. O. Box X
Oak Ridge, TN 37830

R. M. Hamilton
FE-43, GTN
U.S. Department of Energy
Washington, DC 20545

A. Hartstein
FE-43, GTN
U.S. Department of Energy
Washington, DC 20545

L. Headley
Morgantown Energy Technology Center
Morgantown, WV 26505

G. E. Hedstrom
FE-44, GTN
U.S. Department of Energy
Washington, DC 20545

R. Henderson
Lovelace Inhalation Toxicology
Research Institute
P. D. Box 5890
Albuquerque, NM 87115

J. Hill
Ashland Synthetic Fuels, Inc.
P. O. Box 391
Ashland, KY 41101

R. Hill
Ashland Synthetic Fuels, Inc.
P. O. Box 391
Ashland, KY 41101

C. H. Hobbs
Lovelace Inhalation Toxicology
Research Institute
P. O. Box 5890
Albuquerque, NM 87115

J. M. Holland
The Upjohn Company
Kalamazoo, MI 49001

H. L. Hollister
PE-20, FORR
U.S. Department of Energy
Washington, DC 20585

G. R. Holt
ARCO Coal Company
1860 North Lincoln Street
P. O. Box 5300
Denver, CO 80217

H. Hosang
VEBA OEL AG
Postfach 45
4660 Gelsenkirchen-Buer
FEDERAL REPUBLIC OF GERMANY

W. Hubis
4031 South Magnolia Way
Denver, CO 80237

E. L. Huffman
Southern Company Services, Inc.
P. O. Box 2625
Birmingham, AL 35202

S. Ikeda
Japan Coal Liquefaction Development
Co., Ltd.
Rm. 1115, Shuwa Kioi-Cho TBR Bldg.
No. 7, Kojimachi 5-chome,
Chiyoda-Ku, Tokyo 102
JAPAN

J. C. Johnson
FE-13, GTN
U.S. Department of Energy
Washington, DC 20545

T. W. Johnson
Southern Company Services, Inc.
c/o Catalytic, Inc.
P. O. Drawer 239
Wilsonville, AL 35186

W. S. Jones
FE-43, GTN
U.S. Department of Energy
Washington, DC 20545

L. Joseph
Hydrocarbon Research, Inc.
1313 Dolly Madison Blvd.
McLean, VA 22101

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Office of Energy Research
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C. M. Kelly
Air Products and Chemicals, Inc.
Corporate Research and Development
P. O. Box 538
Allentown, PA 18001

S. C. Lewis
Exxon Corporation
Research and Environmental
Health Division
Medical Department
P. O. Box 235
East Millstone, NJ 08873

R. R. Maddocks
Catalytic, Inc.
Centre Square West
1500 Market Street
Philadelphia, PA 19102

A. W. Maki
Exxon Corp.
Research and Environmental
Health Division
P. O. Box 235
East Millstone, NJ 08873

M. J. Massey
Environmental Research and
Technology, Inc.
601 Grant Street
Porter Building, 10th Floor
Pittsburgh, PA 15219

H. McCammon
ER-75, GTN
U.S. Department of Energy
Washington, DC 20545

R. O. McClellan
Lovelace Inhalation Toxicology
Research Institute
P. O. Box 5890
Albuquerque, NM 87115

R. E. McKee
Exxon Corp.
Research and Environmental
Health Division
P. O. Box 235
East Millstone, NJ 08873

P. M. Mehrle
Columbia National Fisheries
Research Laboratory
Route 1
Columbia, MO 65201

M. L. Mendelsohn
Lawrence Livermore Laboratory
University of California
P. O. Box 808
Livermore, CA 94550

J. A. Meyer
Chevron Research Company
P. O. Box 1627
Richmond, CA 94802

L. Miller
FE-42, GTN
U.S. Department of Energy
Washington, DC 20545

M. L. Minthorn
ER-72, GTN
U.S. Department of Energy
Washington, DC 20545

E. C. Moroni
FE-43, GTN
U.S. Department of Energy
Washington, DC 20545

S. C. Morris
Brookhaven National Laboratory
Building 475
Upton, NY 11973

N. B. Munro
Oak Ridge National Laboratory
P. O. Box X
Oak Ridge, TN 37831

P. J. Musser
FE-44, GTN
U.S. Department of Energy
Washington, DC 20545

M. B. Neuworth
The Mitre Corp.
1820 Dolly Madison Blvd.
McLean, VA 22102

J. Norwood
International Coal Refining Co.
P. O. Box 2752
Allentown, PA 18001

M. Parmenter
Kerr-McGee Corporation
Kerr-McGee Center
Packaging & Labeling Dept.
Oklahoma City, OK 73125

R. M. Perhac
Electric Power Research Institute
P. O. Box 10412
Palo Alto, CA 93404

W. Piver
National Institute of Environmental
Health Sciences
P. O. Box 12233
Research Triangle Park, NC 27709

J. D. Potts
Cities Service Research &
Development Co.
Box 3908
Tulsa, OK 74102

J. Reafsnyder
Oak Ridge Operations
U.S. Department of Energy
P. O. Box E
Oak Ridge, TN 37830

C. Reaux
National Institute for Occupational
Safety & Health
Room 117
944 Chestnut Ridge Road
Morgantown, WV 26504

C. A. Reilly
ER-72, GTN
U.S. Department of Energy
Washington, DC 20545

H. Retcofsky
Pittsburgh Energy Technology Center
P. O. Box 10940
Pittsburgh, PA 15236

D. E. Rhodes
Kerr-McGee Corporation
P. O. Box 035
Crescent, OK 73D28

W. J. Rhodes (2)
Industrial Environmental
Research Laboratory
MD-61, US EPA
Research Triangle Park, NC 27711

C. R. Richmond
Oak Ridge National Laboratory
P. O. Box X
Oak Ridge, TN 37830

J. S. Robertson
ER-73, GTN
U.S. Department of Energy
Washington, DC 20545

T. C. Ruppel
Pittsburgh Energy Technology Center
P. O. Box 10940
Pittsburgh, PA 15236

R. Santore
Pittsburgh Energy Technology Center
P. O. Box 10940
Pittsburgh, PA 15236

M. Schulman
ER-70, GTN
U.S. Department of Energy
Washington, DC 20545

A. G. Sharkey
Pittsburgh Energy Technology Center
P. O. Box 10940
Pittsburgh, PA 15236

A. Shepard
American Petroleum Institute
2101 L Street, NW
Washington, DC 20037

D. A. Smith
ER-72, GTN
U.S. Department of Energy
Washington, DC 20545

V. G. Stamoudis
Argonne National Laboratory
9700 South Cass Avenue
Argonne, IL 60439

R. J. Stern
PE-25, FORSTL
U.S. Department of Energy
Washington, DC 20585

J. Stetter
Argonne National Laboratory
9700 South Cass Avenue
Argonne, IL 60439

J. A. Strasser
Atlantic Coal Institute
P. O. Box 1133
Sydney, Nova Scotia
CANADA BIP 6J7

G. Styles
Southern Company Services, Inc.
P. O. Box 2625
Birmingham, AL 35202

R. F. Sullivan
Chevron Research Company
P. O. Box 1627
Richmond, CA 94802

J. W. Thiessen, Deputy Associate
Director
Office of Health and Environmental
Research
ER-71, GTN
U.S. Department of Energy
Washington, DC 20545

G. G. Thurlow
National Coal Board
Coal Research Establishment
Stoke Orchard
Cheltenham, Glos. GL52 4RZ
ENGLAND

R. V. Trense
Exxon Corporation
Environmental Affairs Programs
Exxon Research & Engineering Co.
P. O. Box 101
Florham Park, NJ 07932

A. W. Trivelpiece, Director (3)
Office of Energy Research
ER-1, FORSTL
U.S. Department of Energy
Washington, DC 20585

A. Uzzell
Chevron Research Co.
P. O. Box 7141
San Francisco, CA 94120-7141

G. K. Vick
Exxon Research and Engineering Co.
Route 22 East
Annandale, NJ 08801

W. Wallace
National Institute for Occupational
Safety & Health
Room 117
944 Chestnut Ridge Road
Morgantown, WV 26504

P. Walsh
Oak Ridge National Laboratory
P. O. Box X
Oak Ridge, TN 37830

P. Wambach
PE-241, GTN
U.S. Department of Energy
Washington, DC 20585

W. H. Weber
EPRI
c/o Catalytic, Inc.
P. O. Drawer 239
Wilsonville, AL 35186

K. Wilzbach
Argonne National Laboratory
9800 South Cass Avenue
Argonne, IL 60439

F. E. Witmer
PE-221, GTN
U.S. Department of Energy
Washington, DC 20545

F. J. Wobber
ER-75, GTN
U.S. Department of Energy
Washington, DC 20545

R. W. Wood
ER-74, GTN
U.S. Department of Energy
Washington, DC 20545

A. F. Yen
International Coal Refining Co.
P. O. Box 2752
Allentown, PA 18001

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H. E. Ransom

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