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Characterization of Coal Particles in the Soil of a Former Rail Yard and Urban Brownfield: Liberty State Park, Jersey City (NJ), USA


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1 Characterization of coal particles in the soil of a former rail yard and urban brownfield: Liberty
2 State Park, Jersey City (NJ), USA

3
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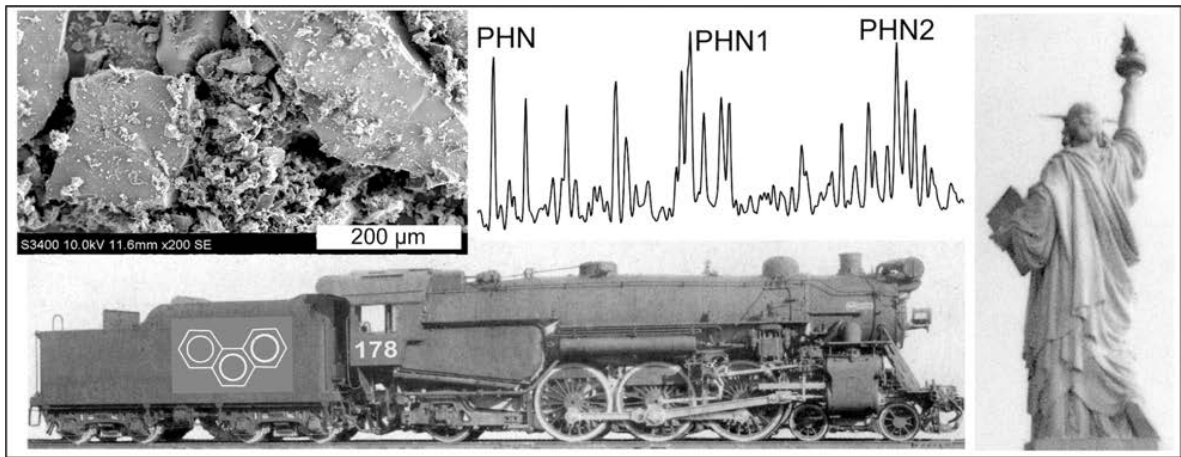
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11 Abstract

12 From the 1850's until the 1960's, the Central Railroad of New Jersey was among several major
13 railways shipping anthracite and bituminous coal to the New York City area, transferring coal
14 from railcar to barge at its extensive rail yard and port facility in Jersey City. The 490 ha Liberty
15 State Park was developed on the site after the rail yard closed, but a ca. 100 ha brownfield zone
16 within the park remains off limits to visitors pending future remediation. As part of an
17 environmental forensic and industrial archeological investigation of this zone, the present study
18 characterizes anthracite and bituminous coal particles present in abundance in the soil by
19 scanning electron microscopy (SEM) and pyrolysis-gas chromatography-mass spectrometry (Py-
20 GC-MS). A simple pretreatment procedure employing density separation improved the
21 analytical results. This detailed information about the nature of contaminants at the site will help
22 to inform the remediation effort in the public interest.

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Graphical abstract

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24 Keywords

25 environmental forensics, coal, Liberty State Park, brownfield remediation, pyrolysis-gas
26 chromatography-mass spectrometry (Py-GC-MS), density separation

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28 Highlights

- 29 • Legacy coal contamination is widespread in the soils of an unremediated restricted area
30 within Liberty State Park (New Jersey, USA), formerly a major rail yard and port for coal
31 shipment.
- 32 • The coal particles in the soil are mostly of anthracite rank, the low PAH content of which
33 reduces the potential environmental hazard at this brownfield site.
- 34 • PAH-rich bituminous coal particles, while less abundant, may be of greater
35 environmental concern, although the degree of bioavailability of their constituent PAHs
36 must be considered.
- 37 • Analysis of soil components by pyrolysis-gas chromatography-mass spectrometry (Py-
38 GC-MS) after a preparative density separation procedure is shown to an effective
39 environmental forensics tool.

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41 Declarations of interest: None

42

43 1. Introduction

44 The Central Railroad of New Jersey (CRRNJ) was one of several major private railways
45 operating from the mid-19th to the mid-20th century with an eastern terminus on New York
46 Harbor and the Hudson River in the U.S. state of New Jersey (Figs. 1, 2). Typical of these

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47 intermodal operations, the CRRNJ transported freight and passengers from the interior to a vast
48 rail yard along the shore for transfer to barges and ferries, respectively, for connection across the
49 water to nearby New York City and points east (Anderson, 1984). Due to unfavorable economic
50 conditions, including competition from highway transportation, all of these private railways
51 ceased operations during the mid-20th century. Some of the lines were subsequently
52 incorporated into the New Jersey Transit regional system, which still maintains a rail-to-ferry
53 passenger service out of the historic station in Hoboken (NJ). CRRNJ's Jersey City station was
54 restored as a tourist attraction but no longer operates, as the tracks were removed when the rail
55 yard was abandoned in the late 1960's and subsequently converted into Liberty State Park (LSP)
56 (Gallagher et al., 2008a; b). The park takes its name from the iconic Statue of Liberty, situated
57 about 600 m across the water at its closest point, allowing park visitors a dramatic view of the
58 rear of the colossus.

Figure 1

Figure 2

61 Coal transport was a major component of CRRNJ operations, for example, producing
62 about 26 % of the company's total revenue in 1943, with 28 % of the coal moving via Pier 18 and
63 its dedicated network of tracks at that time (Figs. 2, 3). The railroad conveyed anthracite coal
64 (Fig. 3A) from its own mines in eastern Pennsylvania and also hauled bituminous coal trains
65 originating further west belonging to other companies. Relative tonnages of anthracite and
66 bituminous coals were roughly the same, varying over time with market demand. Arriving at
67 Pier 18, massive coal dumping structures transferred the cargo to waiting coal barges (Figs. 3B-
68 D) (Anderson, 1984).

Figure 3

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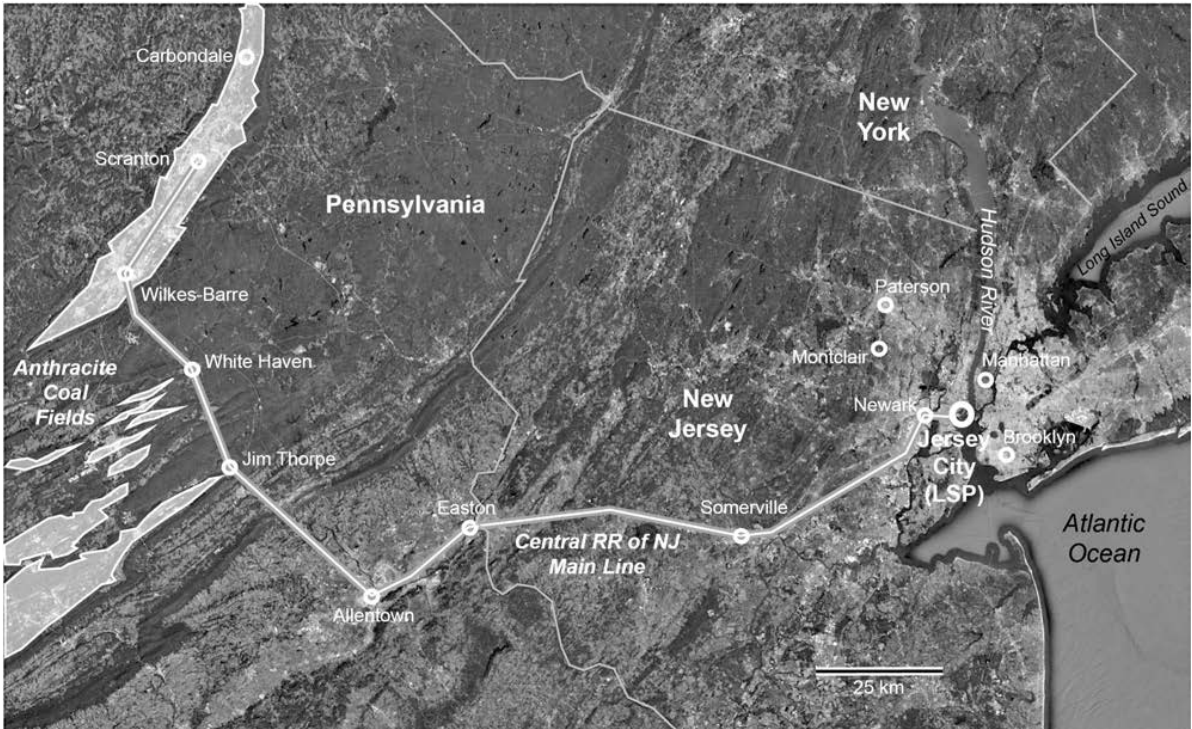


Figure 1. Index map showing location of Liberty State Park (LSP) in Jersey City (NJ), USA, the principal anthracite coal fields of Pennsylvania, and the former Central Railroad of New Jersey main line. Base map: Google Earth; coalfields: Pennsylvania Dept. of Environmental Protection; rail line: Anderson (1984).

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Figure 2. The Central Railroad of New Jersey's rail yard and marine terminal in Jersey City as it appeared in a 1954 aerial image, overprinted with the location of the two soil samples (25R, 43) presented in this study. At the time of the photograph, coal transport operations were largely confined to the zone seen in the lower part of the image, on the tracks leading to Pier 18. Note the locations of the passenger terminal and roundhouse. Base image: U.S. Geological Survey; identification of coal handling facilities: Anderson (1984); pier identification: Brooklyn Historical Society Archives.

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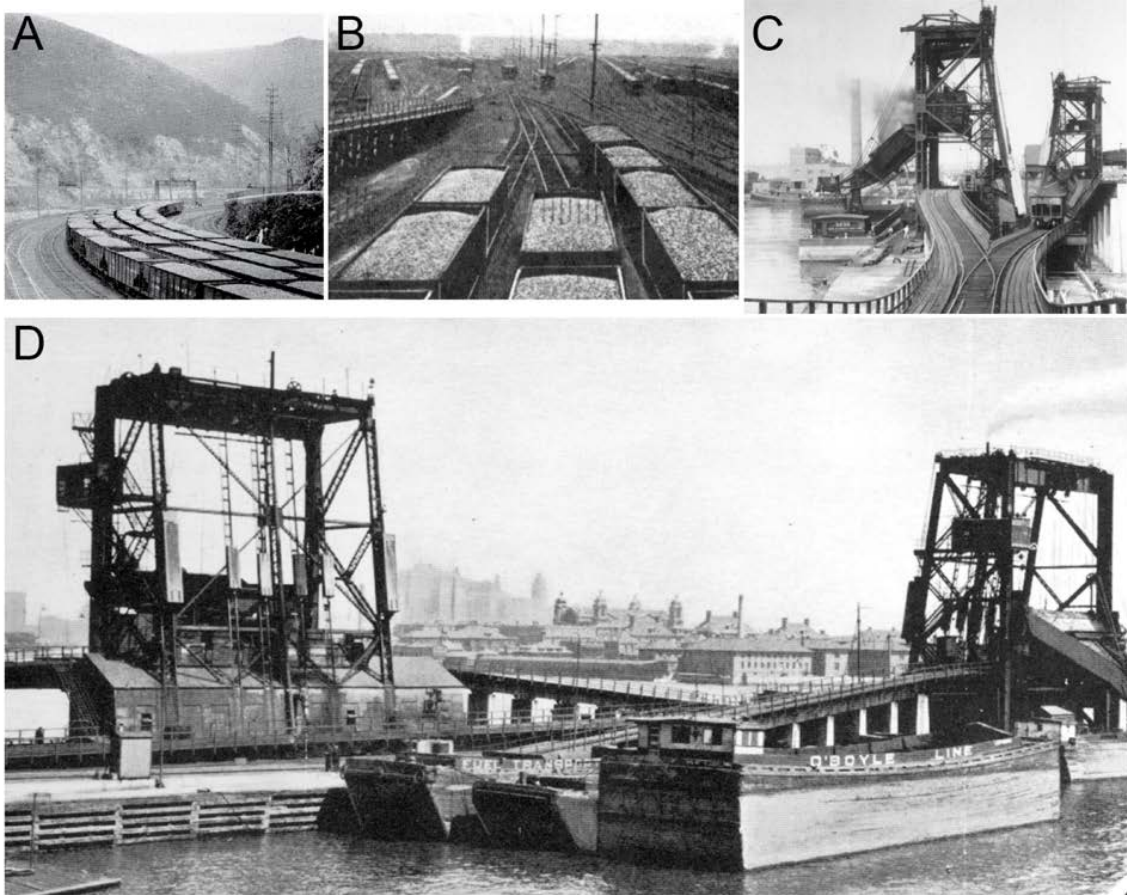


Figure 3. Historical images of CRRNJ coal transport operations in the 1940's. (A) Loaded coal trains in Jim Thorpe, Pennsylvania (Fig. 1; town formerly known as Mauch Chunk). (B) Loaded coal cars approach Pier 18 in the Jersey City rail yard. View to the west showing the yard's track network (Fig. 2). (C) View of Pier 18's two coal dumping towers for transfer of coal from railcar to barge. View is to the west from the eastern end of the pier. (D) View to the northeast of Pier 18's coal dumpers. Note Ellis Island in the background. Photos: Anderson (1984); used with permission.

(2 Column)

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395 70 After the rail yard and its piers were closed and dismantled, the state of New Jersey
396
397 71 acquired the land and created the 490 ha Liberty State Park. About 100 ha of the park remains
398
399 72 an unremediated brownfield site, off limits to the public and constituting the study area of this
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401 73 project (Fig. 4A). In recent years, the site's botanical succession, soil microbiology, and
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403 74 contaminant geochemistry have been extensively studied (e.g., Gallagher et al., 2008a; b; 2018;
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405 75 Haggmann et al., 2015; 2019; Krumins et al., 2015; Singh et al., 2019a; b). In spite of evident
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407 76 inorganic and organic contamination, including abundant visible coal fragments in the soil, most
408
409 77 of the restricted zone supports lush plant life, the product of natural, passive revegetation over a
410
411 78 half century (Figs. 4B, C).

414 79 Figure 4

416 80 Unburned coal, particularly of high volatile bituminous rank, contains high
417
418 81 concentrations of polycyclic aromatic hydrocarbons (PAHs) among other compounds (Stout and
419
420 82 Emsbo-Mattingly, 2008; Laumann et al., 2011). While PAHs in soils may affect plant health
421
422 83 (Brooks, 2004; Smith et al., 2006), the extent to which this is an environmental concern in this
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424 84 case is linked to the degree of PAH bioavailability and biodegradability if sequestered within
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426 85 coal particles in soil (Stout and Emsbo-Mattingly, 2008; Yang et al., 2008a; b; Achten and
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428 86 Hofmann, 2009; Achten et al., 2011; Fabiańska et al., 2016; Hindersmann and Achten, 2018;
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430 87 Nádudvari et al., 2018a; b). Haggmann et al. (2019) undertook an environmental forensic
431
432 88 investigation of coal-contaminated soils from the LSP brownfield site, describing in detail the
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434 89 distribution of saturated and aromatic hydrocarbons, heavy metals, and coal macerals. However,
435
436 90 they used only the < 2 mm particle size fraction, to the exclusion of the visible coal particles
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438 91 evident during field sampling. The present study re-examines soils from two of the investigated
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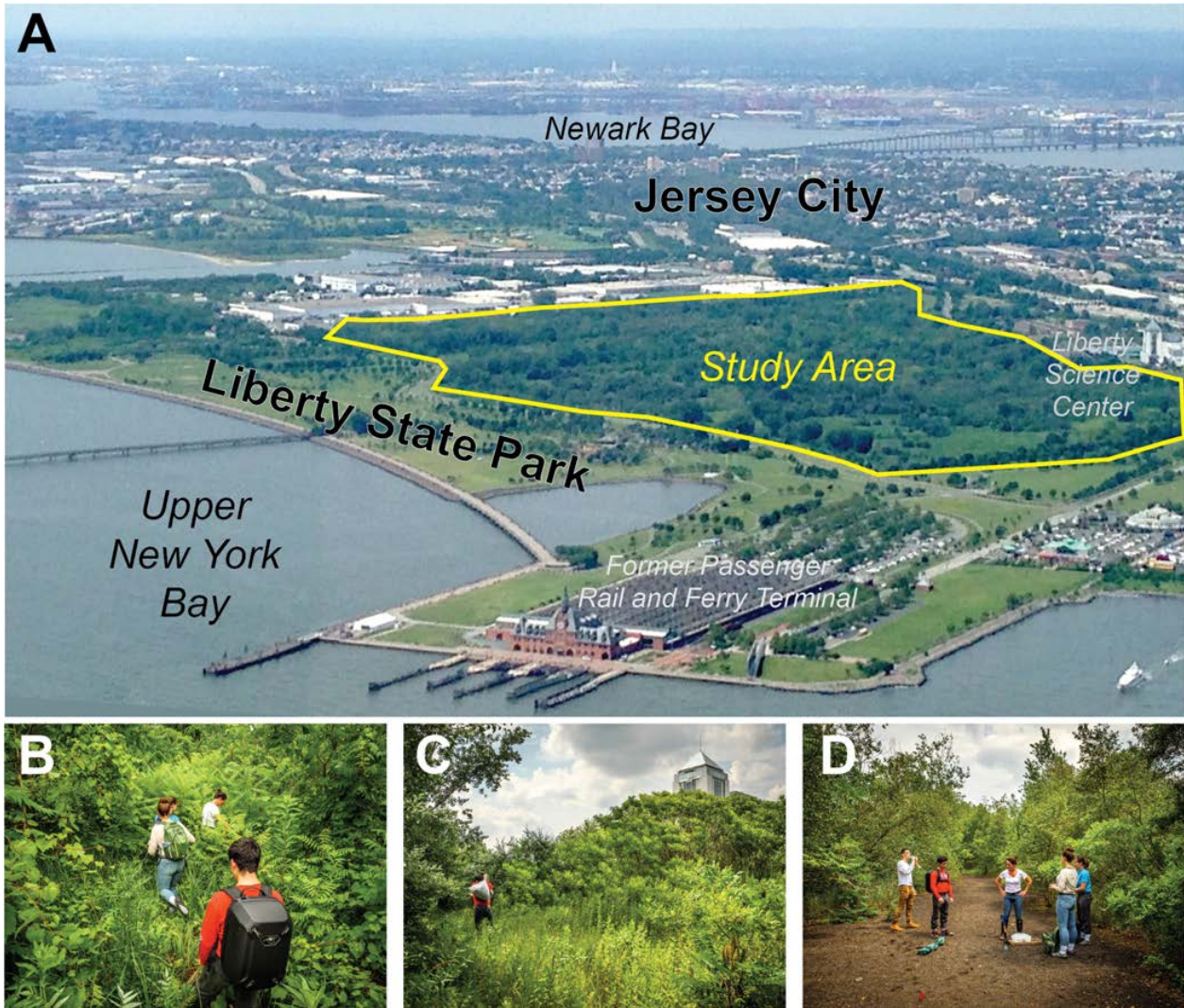


Figure 4. Appearance of Liberty State Park in 2017. (A) Aerial view towards the southwest showing the study area within the park. Note the former passenger rail and ferry terminal, partially restored but non-functioning, and the Liberty Science Center museum, built on the site of the former railroad roundhouse (Fig. 2). Photo: D. Haggmann. (B, C) Dense vegetation covers most of the study area. The top of the Liberty Science Center tower appears in C. (D) Soil sample 25R was collected from this anomalously barren strip within the study area. Photos B-D: M. Peters, Montclair State Univ.; used with permission.

(2 Column. Grayscale in print edition; color in online edition.)

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92 sampling locales within LSP (Fig. 2), this time considering the full particle size range with
93 emphasis on coal, to aid in future remediation of the brownfield.

94 Micro-scale analytical pyrolysis-gas chromatography-mass spectrometry (Py-GC-MS)
95 has been shown to provide a rapid, reproducible means of chemically characterizing a wide
96 variety of solid organic matter types with minimal sample preparation (Wampler, 2007). Py-GC-
97 MS has increasingly been applied to environmental investigation of soils and sediments
98 (summarized in Kruge, 2015), specifically including brownfield studies (Lara-Gonzalo et al.,
99 2015) and environmental forensics (Krugue et al., 2018). It is utilized here for the direct,
100 qualitative characterization of coal particles and coal-contaminated soil.

101 Sedimentary petrologists have long favored density separation for isolating heavy
102 minerals from sandstones for microscopic evaluation (e.g., Boggs, 2009). It has also been
103 employed extensively in coal studies, evolving into the use of the sophisticated analytical
104 technique of density gradient centrifugation for the separation of coal and kerogen macerals (e.g.,
105 Dyrkacz and Horwitz, 1982; Crelling, 1988; 1989; Stankiewicz et al., 1994a;b; Krugue et al.,
106 1997). In the present study, a simple floatation method was employed to isolate soil organic
107 matter and various coal types to improve the chemical characterization results.

108 The restricted zone of LSP is slated for gradual remediation into managed wetland,
109 grassland, and forest with public access (McDonald, 2018). The environmental forensic and
110 industrial archeological approach of the present study will help to inform the remediation effort
111 in the public interest.

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113 2. Methods
114 2.1. Site description

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115 Soils for this study were collected within LSP in Jersey City (NJ, USA) include soil from
116 vegetated Site 43, formerly beneath a railroad track, and soil from Site 25R taken on what
117 remains an anomalously barren strip of land formerly between railroad tracks (Figs. 1-4). These
118 sites are inside the unremediated, restricted-access 100-ha zone of the park. The railroad tracks
119 and their crossties were removed around the time the railyard was abandoned in the late 1960s.
120 Since the railyard was abandoned, a dense forest consisting mostly of hardwood and herbaceous
121 assemblages naturally grew within the restricted-access area (Gallagher et al., 2008a; b) (Figs.
122 4A-C).

123 2.2. Soil collection

125 Soil was collected from LSP sites 43 and 25R from below the leaf litter to a depth of 10
126 cm and stored in at 4 °C. Sample coordinates were determined by reference to Global
127 Positioning System (GPS) satellite signals in the field, transferred to aerial imagery using the
128 Google Earth application, and carefully matched by graphical overlay to the 1954 aerial image
129 (Fig. 2) in the U.S. Geological Survey archives (earthexplorer.usgs.gov) as previously detailed
130 (Hagmann et al., 2019).

131 2.3. Hand-picked coal and plant material

133 Vegetation detritus from LSP site 43 was hand-picked from whole soil. This plant
134 material, which consisted of roots and twigs, were rinsed in deionized (DI) water and dried (40
135 °C overnight). In another procedure, soil samples from sites 25R and 43 were wet-sieved
136 through a 2 mm sieve and sonicated in DI water. The > 2 mm fraction was further separated into
137 the following categories based on visual inspection under a binocular microscope: coal, coke,

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138 and combustion spherules. Coal particles from both sites (2 to 10 mm in size) were designated
139 for further processing, as described in Sections 2.4 and 2.6 (Fig. 5).

Figure 5.

2.4. Scanning electron microscopy (SEM)

142 Before SEM, the hand-picked coal particles were individually air-dried and gently
143 crushed using a mortar and pestle. Fragments of a single coal particle were spread on the carbon
144 tape and then loaded on the SEM sample stub. After applying a thin layer of carbon film under a
145 Denton Desk 4 coater, the fragments were observed by the Hitachi S-3400N SEM and with
146 Bruker –AXS Energy Dispersive X-Ray Spectroscopy (EDS) detector.

2.5. Soil separation by density

149 Soils from both sites were also separated based on density (Fig. 5). First, dried whole
150 soil (40 °C overnight) was ground using a mortar and pestle to pass through a 1 mm sieve. A 5 g
151 aliquot was placed in 10 mL of DI water (1.0 g/mL) and the floating material after centrifugation
152 was collected (Fraction 1). An aqueous potassium iodide (ACS Reagent Grade, Ricca Chemical,
153 Fisher Scientific) solution (1.6 g/mL in DI water, 10 mL) was added to the remaining soil (i.e.,
154 the sink material after Fraction 1 was removed). The particles that were floating after
155 centrifugation were collected in filter paper and rinsed with DI water (Fraction 2). Finally, the
156 remaining residue was rinsed with DI water and collected (Fraction 3). For each fraction, the
157 suspension was thoroughly mixed and then centrifuged at 4,000 rpm for 15 minutes. Aliquots of
158 Fraction 3 residues were analyzed by SEM, following the procedure outlined in Section 2.4.
159 Fraction 1 was predicted to contain the natural biomass that floats in water, Fraction 2 was

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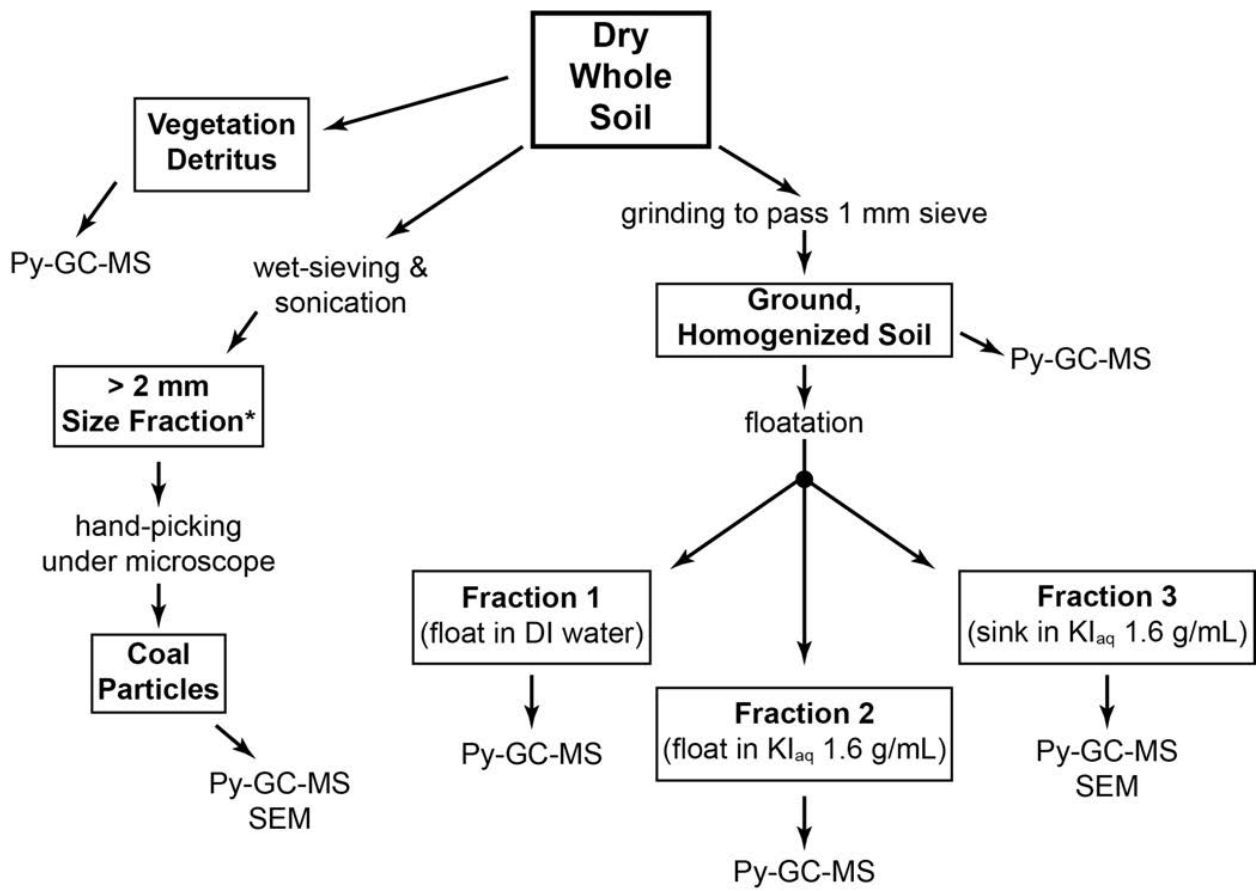


Figure 5. Experimental flow chart. See section 2 for details. No vegetation detritus was picked from barren site 25R soil. * < 2 mm size fraction previously studied in detail (Hagmann et al., 2019).

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160 expected to include the coal particles that float in the dense aqueous KI solution, while Fraction
161 3 should include the soil mineral matter that is too dense to float in either liquid.

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163 2.6. Pyrolysis-Gas Chromatography-Mass Spectrometry (Py-GC-MS)

164 The hand-selected vegetation detritus was crushed using a mortar and pestle and analyzed
165 by Py-GC-MS (Fig. 5). Several of the hand-picked coal particles were individually crushed
166 using a mortar and pestle and separately analyzed by Py-GC-MS. These included ten individual
167 coal particles from site 43 and three coal particles from site 25R. Whole soil samples and each
168 of the three fractions separated by density from LSP sites 43 and 25R were also pyrolyzed. For
169 quality control, Py-GC-MS of the 25R whole soil was performed twice. Py-GC-MS was
170 accomplished using a CDS 5150 Pyroprobe (CDS Analytical Inc., Oxford, PA) coupled to a
171 Thermo Finnigan Focus DSQ GC/MS (Thermo Electron Corporation, Madison, WI) equipped
172 with an Agilent DB-1MS column (30 m × 0.25 mm i.d. × 0.25 μm film thickness). The GC oven
173 temperature was programmed from 50 °C to 300 °C (at 5 °C min⁻¹), with an initial hold of 5 min
174 at 50 °C and a final hold of 15 min at 300 °C. Pyrolysis was performed for 20 s at 610 °C. The
175 MS was operated in full scan mode (50-500 Da, 1.08 scans s⁻¹). The MS was calibrated by
176 autotuning with PFTBA and blanks were run each day before samples were analyzed.
177 Compounds were identified using the W8N08 mass spectral library (John Wiley and Sons, Inc.,
178 New York, NY), the online NIST Standard Reference Database Number 69
179 (webbook.nist.gov/chemistry/), and by reference to the literature. For this study, no internal or
180 external standards were employed, thus no attempts at quantitative determination were made.

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182 3. Results and discussion

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787 183 3.1. SEM of coal particles
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789 184 Hand-selected coal particles from the > 2 mm fraction of soil from LSP site 43 were
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791 185 imaged using SEM, revealing surface encrustations that had resisted sonication (Fig. 6). The
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793 186 EDS mapping indicated that the encrustations like those imaged in Figure 7 are aluminosilicate
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795 187 phases (strong Si, Al, and O spectral signals) adhering to the coal. The overlapping spectral
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797 188 signals (Fig. 7B) can more clearly be seen in the individual mapping of Al and Si (Figs. 7C, D).
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799 189 Other hand-picked coal particles from LSP sites 43 and 25R produced similar SEM images. EDS
800
801 190 also detected Fe and S in molar abundances roughly the same as those of Si and Al.
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803

804 191 Figure 6

805
806 192 Figure 7

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808 193 Using organic petrography, Haggmann et al. (2019) demonstrated that the < 2 mm size
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810 194 fraction of the site 43 soil contained about 32 % detrital clay by volume. It is likely therefore
811
812 195 that the aluminosilicate phases observed by SEM are clays. EDS spectra show approximately
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814 196 equal molar amounts of Si and Al, as well as an absence of K and Na. This suggests that the
815
816 197 observed clays are most likely kaolinite (Welton, 1984). The iron and sulfur might be present as
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818 198 pyrite or a weathered derivative, however this was not confirmed petrographically.
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820
821 199 The aluminosilicate clay encrustations present on the site 43 and 25R coal particles, such
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823 200 as those seen in Figures 6 and 7, have been interpreted as hallmarks of coal weathering in that
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825 201 oxidation allows clay minerals to better adhere to the coal surface (Xia et al., 2014, Xia & Yang,
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827 202 2014). The LSP samples are from the top 10 cm of the soil profile. Thus, the coal particles were
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829 203 likely subjected to weathering over a half century or more, having been exposed to atmospheric
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831 204 O₂ in soil pore spaces, infiltrating meteoric water, seasonal temperature swings, and action by
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833 205 resident soil microbes. If the coal particles had been weathered chemically as well as physically,
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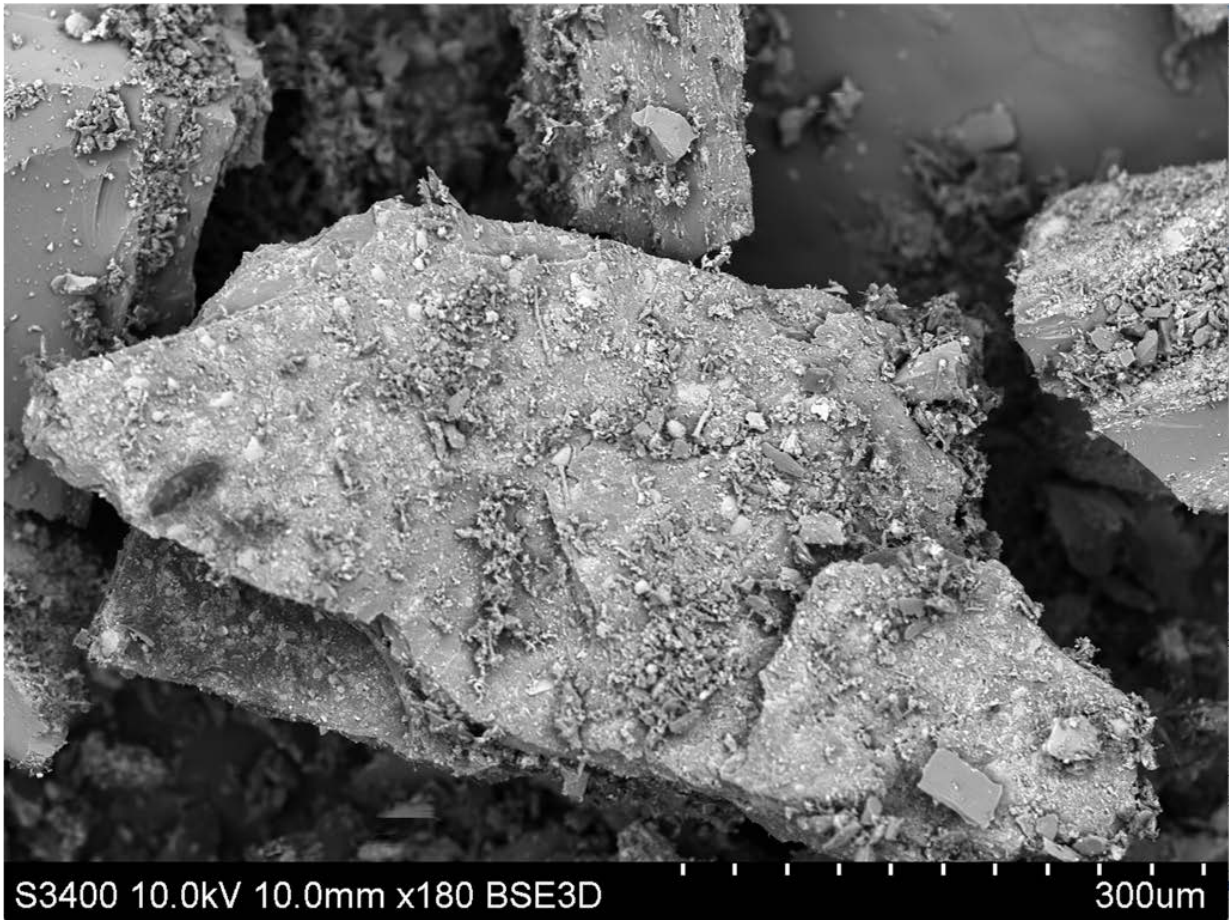


Figure 6. Scanning electron micrograph of fragments of a single wet-sieved (> 2 mm) and sonicated LSP 43 coal particle. Note surface encrustations. Scale bar is 300 μm .

(One column.)

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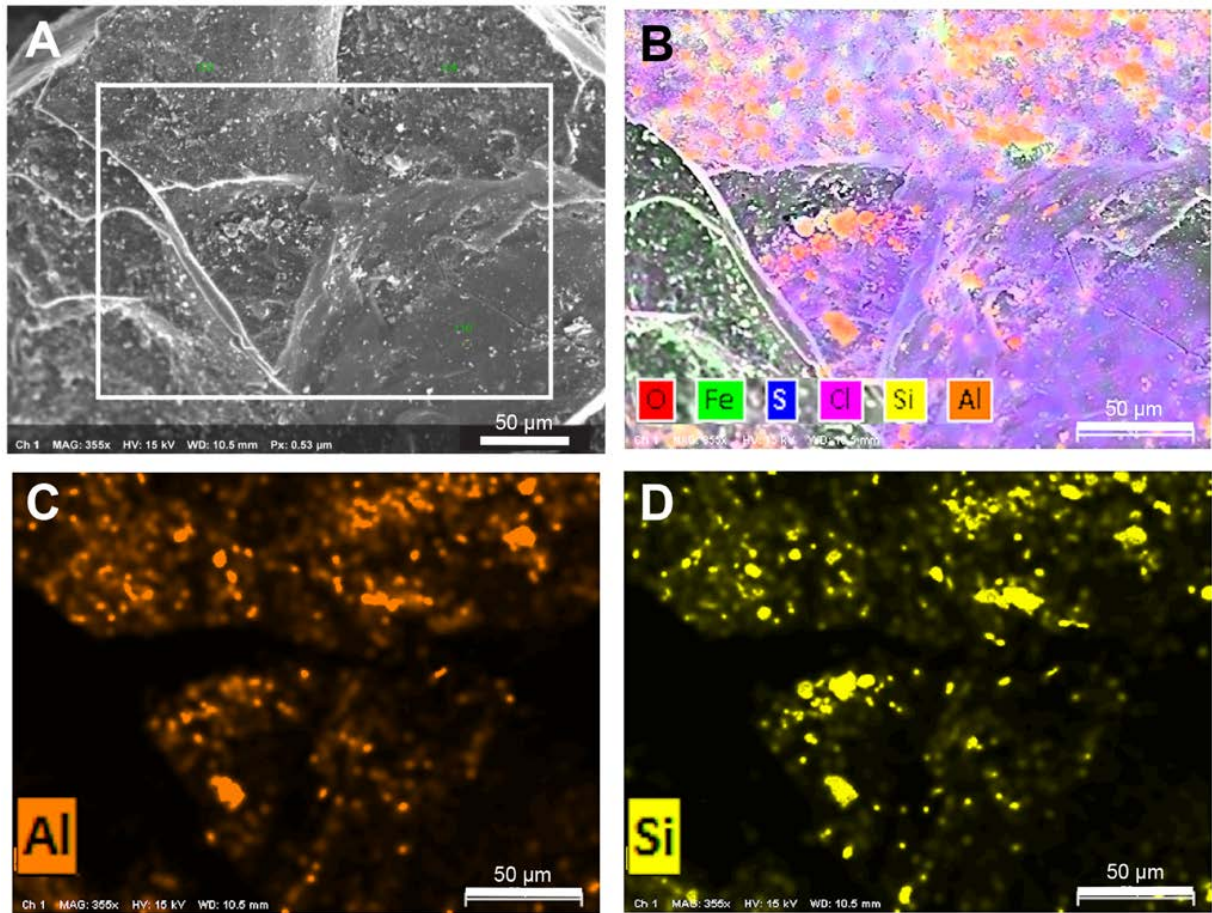


Figure 7. SEM EDS mapping images of a fragment of a single wet-sieved (>2 mm) and sonicated LSP 43 coal particle. Scale bars are 50 μm. (A) SEM image; box shows element mapping area for B-D. (B) Multi-element map (O, Fe, S, Cl, Si, Al) superimposed on SEM image. (C) Element map for aluminum. (D) Element map for silicon. Element mapping images indicate clay mineral platelets adhering to coal.

(Two column. Grayscale in print edition; color in online edition.)

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206 their composition would obviously have been affected. The particles were therefore subjected to
207 chemical analysis in part to determine if this indeed had been the case (Sec. 3.2).

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209 3.2. Py-GC-MS of coal particles and plant material

210 The pyrolysis products of the vegetation detritus from site 43 included lignin marker
211 compounds [methoxyphenols, labeled as chromatographic peaks L1-L15], polysaccharide
212 derivatives [P1-P6], phenols [F1-F3], long-chain aliphatic hydrocarbons [^], steroids [S1, S2],
213 and triterpenoids similar to β -amyrone [BAM] (Fig. 8A, Table 1). Ten coal particles were
214 analyzed by Py-GC-MS. Nine of them had pyrograms resembling the one in Figure 8B,
215 essentially showing only the simple monoaromatic hydrocarbons benzene [A1], toluene [A2],
216 and alkylated benzenes [A3-A6]. Only one out of ten site 43 coal particles had a distinctly
217 different pyrogram (Fig. 8C). This much more complex pyrolyzate, in addition to the
218 monoaromatics [A1-A7], contained phenol and alkylated phenols [F1-F8], dibenzofuran [DBF],
219 alkylated dibenzofurans [DBFx], parent and alkylated PAHs including naphthalenes [Nx],
220 phenanthrenes [PHNx], fluorene [FLU], pyrenes [PYRx], and chrysenes [CHRx]. The alkylated
221 PAHs were relatively more abundant than the parent compounds, and pristane predominated
222 over phytane.

223 Figure 8

224 Table 1

225 The lignin and polysaccharide marker compounds present in the pyrolyzate of the plant
226 material (Fig. 8A), which is comprised of roots and twigs, are those typical of vegetation and
227 forest soil biomass (e.g., Saiz-Jiménez & de Leeuw, 1986; Hempfling & Schulten, 1990; Kuder
228 & Krüge, 1998; Kuroda & Nakagawa-izumi, 2006). The steroids and triterpenoids likely derive

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Forested Site 43
Py-GC-MS Total Ion Current

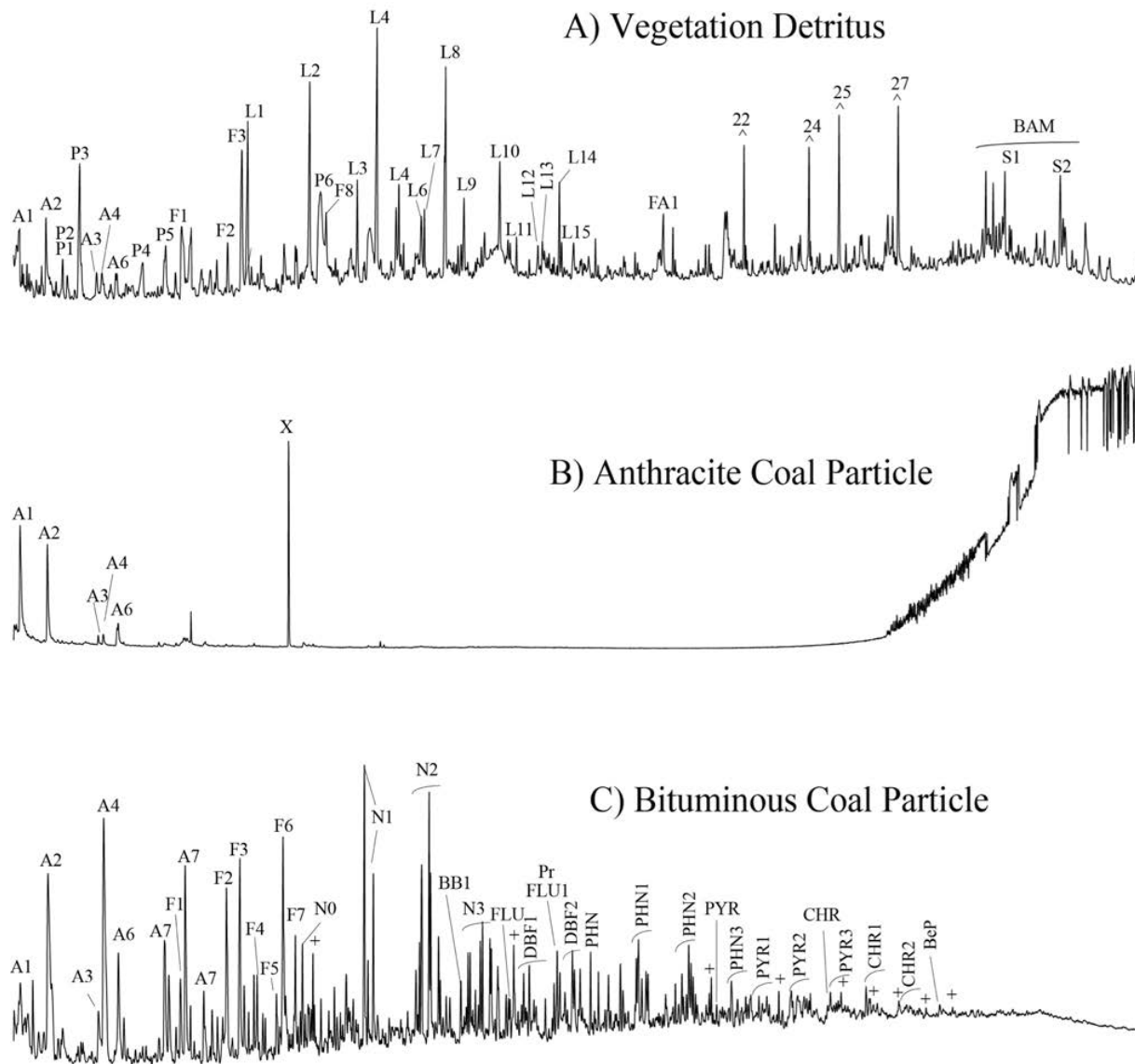


Figure 8. Py-GC-MS total ion current chromatograms of materials from the site 43 soil sample: (A) typical soil organic matter (roots & twigs) and (B, C) two coal particles hand-picked from the >2 mm size fraction after wet sieving and sonication. See Table 1 for peak identification.

(Two column.)

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Table 1. Pyrolysis-GC-MS peak identification for Figures 8-10.

<u>Aliphatic Hydrocarbons</u>		<u>Polysaccharide markers</u>	
+	n-alkanes	P1	furan-3-one
^	n-alk-1-enes	P2	2-furancarboxaldehyde
pr	pristane	P3	3-furancarboxaldehyde
<u>Monoaromatic Compounds</u>		P4	methylfuranone
A1	benzene	P5	methylfurancarboxaldehyde
A2	toluene	P6	benzenediol
A3	ethylbenzene	<u>Lignin markers</u>	
A4	meta- & para-xylene	L1	guaiacol
A5	styrene	L2	methylguaiacol
A6	ortho-xylene	L3	ethylguaiacol
A7	C3-alkylbenzene	L4	vinylguaiacol
A8	benzaldehyde	L5	eugenol
A9	benzonnitrile	L6	vanillin
<u>Polycyclic aromatic compounds</u>		L7	cis iso-eugenol
Nx	naphthalenes	L8	trans iso-eugenol
BBx	biphenyls	L9	acetovanillone
DBFx	dibenzofurans	L10	vinylsyringol
PHNx	phenanthrenes	L11	prop-1-enyl syringol
FLUx	fluorenes	L12	prop-2-enyl syringol (cis)
FLA	fluoranthene	L13	syringaldehyde
PYRx	pyrenes	L14	prop-2-enyl syringol (trans)
BAN	benzo[a]anthracene	L15	acetosyringone
CHRx	chrysenes	<u>Fatty acids</u>	
BeP	benzo[e]pyrene	FA1	n-hexadecanoic acid
(x indicates extent of alkyl substitution)		FA2	n-octadec-9-enoic acid
<u>Phenols</u>		FA3	n-octadecanoic acid
F1	phenol	<u>Steroids</u>	
F2	2-methylphenol	S1	stigmastan-3,5-diene
F3	3-methylphenol & 4-methylphenol	S2	stigmasta-5-en-3-ol
F4	2-ethylphenol	S3	stigmasta-3,5-dien-7-one
F5	2,4-dimethylphenol	S4	stigmasta-4-en-one
F6	4-ethylphenol	S5	stigmasta-4,22-dien-3-one
F7	3-ethylphenol & 3,5-dimethylphenol	<u>Other</u>	
F8	vinylphenol	BAM	terpenoids similar to β -amyrone (C ₃₀ H ₄₈ O) or derivative
F9	trimethylphenol isomers	DKDP	diketodipyrrole
		X	contaminant introduced during processing

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1123 229 from the plant matter and/or soil microbes (Hagmann et al., 2019). Fresh and degraded plant
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1125 230 materials obviously constitute important, non-contaminant soil components, which furthermore
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1128 231 produce strong pyrolytic signatures. In their prior study, Hagmann et al. (2019) pyrolyzed whole
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1130 232 LSP soils, yielding results in which the contaminant signals were mixed with those of the natural
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1132 233 vegetation present. One objective of the present study is the isolation of the coal contaminant
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1134 234 signatures from that of the plant material, for which the first step is the characterization of the
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1136 235 individual components. The next step (Section 3.3) is the experimental attempt to isolate these
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1138 236 soil constituents by density separation.

1140 237 It was assumed that the coal particles hand-picked from the soil samples (Sec. 2.3) would
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1142 238 include coals of different ranks since the historical record documents bulk transport of
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1144 239 bituminous and anthracite by coal-fired locomotives (Anderson, 1984). One coal particle (Fig.
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1146 240 8B) produced simple alkylated benzenes nearly exclusively upon pyrolysis, consistent with
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1148 241 previously documented anthracite coal pyrolyzates (Xu et al., 2017). Organic petrography
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1150 242 indicated the presence of inertinite-dominant coal particles in soil samples from Site 43
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1152 243 (Hagmann et al., 2019) but inertinite pyrolysis products are considerably more complex
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1154 244 (Stankiewicz et al., 1994a). Therefore, this coal particle and the other eight yielding similar
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1156 245 pyrograms are all deemed to be anthracite by their distinctive pyrolytic fingerprint (although in
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1158 246 the absence of confirmation by organic petrology or proximate and ultimate analysis). The
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1160 247 sample shown in the SEM images (Figs. 6, 7) is one of these eight particles. About 70 % of the
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1162 248 coal at this site was previously determined to be anthracite by petrographic examination
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1164 249 (Hagmann et al., 2019), so it would not be surprising that most of the hand-picked coal particles
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1166 250 in the present study would be anthracite.

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1179 251 Pyrolysis products from the remaining coal particle (Fig. 8C) closely resemble those of
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1181 252 bituminous coal (Hatcher et al., 1992; Kruge & Bensley, 1994; Stankiewicz et al., 1994a; b;
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1183 253 Laumann et al., 2011). These authors attest to the singular importance of oxygenated
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1185 254 compounds in high-volatile bituminous coal pyrolyzates, in particular the phenols, as well as
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1187 255 secondary amounts of dibenzofurans. These compounds are clearly evident in this particle's
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1189 256 pyrolyzate [F1-F7, DBF1, DBF2]. Alkyl naphthalenes are also important components of
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1191 257 bituminous coal pyrolyzates (Hatcher et al., 1992; Kruge & Bensley, 1994; Stankiewicz et al.,
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1193 258 1994a) and are among the most abundant [N0-N3] in the present example (Fig. 8C). These same
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1195 259 authors also demonstrated that pyrolytic phenols predominate when analyzing vitrinite of lower
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1197 260 rank high volatile bituminous coals. However, in pyrolyzates of coals of increasing rank, the
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1199 261 relative importance of the phenols is progressively reduced, while both parent and alkylated
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1201 262 PAHs become more evident (Krug & Bensley, 1994; Laumann et al., 2011). Although phenols
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1203 263 [F1-F7] are very significant components in the present case (Fig. 8C), the prevalence of
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1205 264 naphthalenes [N0-N3], and larger parent and alkyl-PAHs including the phenanthrenes [PAHx],
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1207 265 pyrenes [PYRx], and chrysenes [CHRx] suggest that this is likely to be a higher rank bituminous
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1209 266 coal. Previous petrographic examination (Hagmann et al., 2019) indicated that 17 % of the coal
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1211 267 in the site 43 soil was medium volatile bituminous while only 8 % was high volatile. The
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1213 268 particle in this case (Fig. 8C) is likely to be medium volatile based on its pyrolytic signature.
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1215 269 Pyrolysis did not reveal marked evidence of chemical weathering, such as oxygenated PAHs.
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1221 271 3.3. Density separation of soil

1222 272 Whole soils from vegetated site 43 and barren site 25R were separated into three fractions
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1224 273 based on density (Fig. 5, Table 2). To achieve a clean signal for the coal Py-GC-MS
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1235 274 fingerprints, the plant material, predicted to be Fraction 1, needed to be separated from the coal
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1237 275 particles, expected in Fraction 2, as explained in Section 3.2. The residue material anticipated in
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1239 276 Fraction 3 was anticipated to confirm that the coal particles had been successfully isolated in
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1241 277 Fraction 2. The site 25R soil yielded only 0.06 % by weight of light Fraction 1 while site 43
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1243 278 yielded 0.39 %. LSP site 43 had more of the intermediate Fraction 2 (3.10 %) compared to site
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1245 279 25R (0.89 %). For both sites, most of the material remained in the heavy third fraction (92.6 and
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1247 280 95.9 %, respectively, for 43 and 25R).

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1250 281 Table 2

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1252 282 Previous work (on the < 2 mm size fraction) indicated that the LSP soil samples were rich
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1254 283 in organic matter (soil biomass plus coal, coke and char). Site 43 soil was found to consist of
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1256 284 about 30 % by weight of organic matter, while 25R had about 11 % (Hagmann et al., 2019).
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1258 285 Therefore, the low Fraction 1 and 2 yields (Table 2) appear incongruous at first glance. With
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1260 286 bituminous coal and anthracite having specific densities of 1.32 and 1.47 g/mL, respectively
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1262 287 (Flores, 2013; Wood et al., 1983), the KI solution with a density of 1.6 g/mL employed in the
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1264 288 present experiment was expected to be adequate for the floatation of both types of coal.
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1266 289 However, based on the SEM observations (Figs. 6, 7), stubbornly adhering mineral phases
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1268 290 evidently precluded a complete isolation of coal fragments by density, relegating most of the
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1270 291 material to the third (residual) fraction (Table 2). Adhering or embedded minerals increase the
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1272 292 bulk density of the coal particles, perturbing the outcome of float-sink procedures (Garcia et al.,
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1274 293 1991; Stankiewicz et al., 1994b; Suárez-Ruiz & Crelling, 2008). SEM examination of the
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1276 294 residual fraction did indeed reveal abundant, widely-distributed mineral matter for both soil
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1278 295 samples. A more rigorous attempt to isolate the organic materials from the minerals by a
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1280 296 micronization pretreatment was beyond the scope of this project.

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Table 2. Dry weight percentages of density fractions separated from whole soil of LSP Sites 43 and 25R. See text and Figure 5 for procedural details.

Soil	Total soil dry weight	Fraction 1 (floated in DI water)	Fraction 2 (floated in 1.6 g/mL KI _{aq})	Fraction 3 (sank in 1.6 g/mL KI _{aq})
43	5.007 g	0.39 %	3.10 %	92.58 %
25R	5.046 g	0.06 %	0.89 %	95.94 %

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298 3.4. Py-GC-MS of soil density fractions

299 To investigate their organic chemical composition in detail, whole soil and each density
300 fraction were subjected to Py-GC-MS (Fig. 5). Results from the two field sites are presented
301 separately.

302

303 3.4.1. Forested site 43 soil

304 Upon pyrolysis, forested site 43's whole soil revealed a predominance of simple
305 alkylbenzenes and naphthalenes [A1-A7, N0-N3] (Fig. 9A). Notable minor components include
306 polysaccharide and lignin marker compounds [P1-P3, L1], phenols [F1-F5], dibenzofurans
307 [DBFx], PAHs [FLUx, PHNx, FLA, PYR, CHR], diketodipyrrole [DKDP] and long-chain *n*-
308 alkanes [+]. Hagemann et al. (2019) noted a greater prevalence of polysaccharide and lignin
309 markers, as well as phenols in site 43 soil pyrolyzates, but it must be kept in mind that they
310 analyzed only the < 2 mm soil size fraction. The site 43 density Fraction 1 pyrolyzate is
311 distinctly different from the whole soil, with lignin and polysaccharide markers dominant [L1-
312 L15, P1-P6], along with phenols [F1-F8], diketodipyrrole [DKDP], fatty acids [FA1-FA3], long-
313 chain *n*-alkenes [^], and sterols [S1, S2] (Fig. 9B).

314

Figure 9

315 The complex pyrolyzate of Site 43's Fraction 2 has an overwhelmingly aromatic
316 signature (Fig. 9C). Significant compounds include monoaromatic hydrocarbons [A1-A7],
317 phenols [F1-F8], naphthalenes [N0-N3], dibenzofurans [DBFx], and parent and alkylated PAHs
318 [FLU1, PHNx, PYRx, CHRx, BeP]. *n*-Alkanes [+] and triterpenoids [BAM] are also
319 noteworthy. In contradistinction, Fraction 3 produced mostly monoaromatic hydrocarbons [A1-

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Forested Site 43
Py-GC-MS Total Ion Current

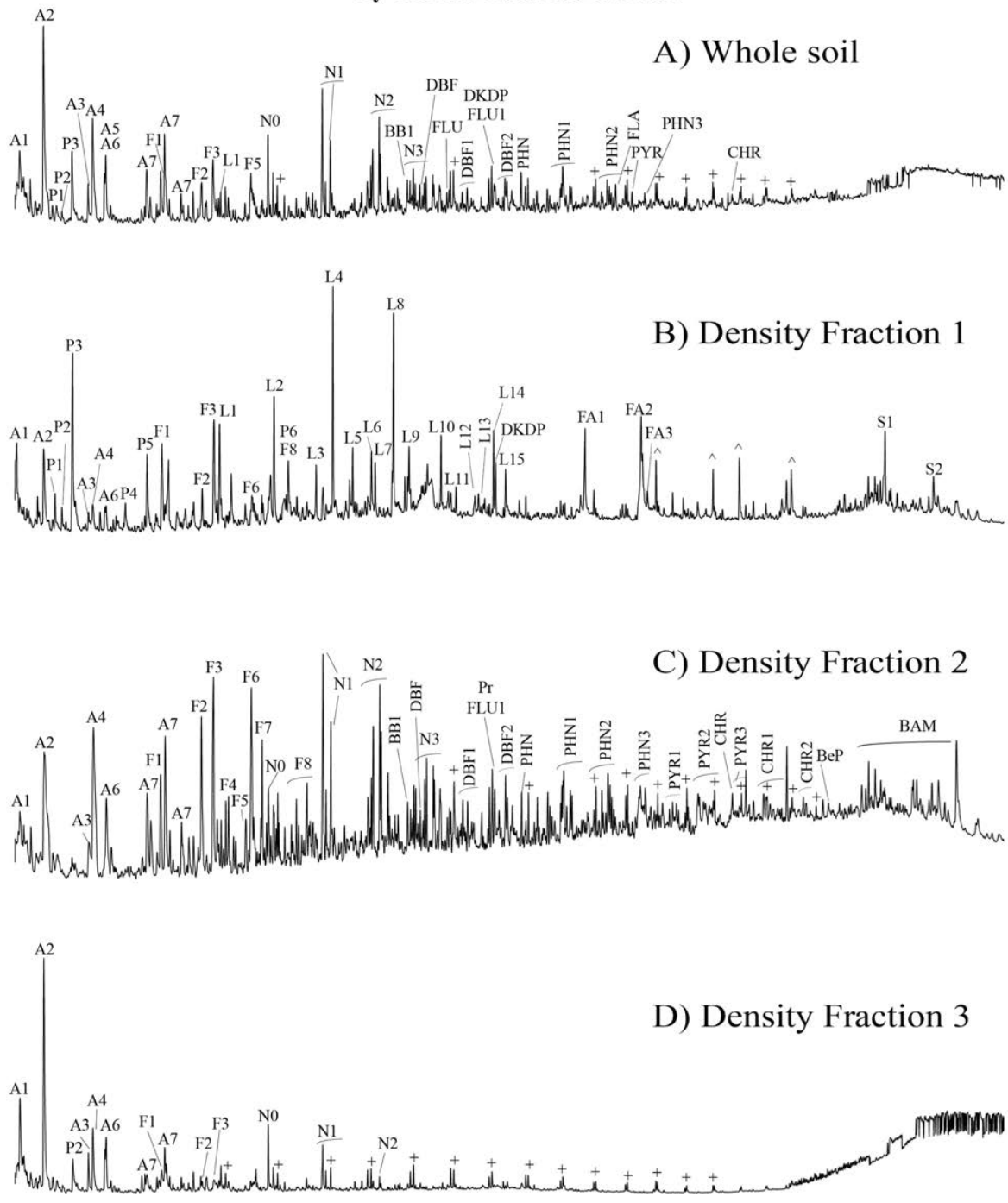


Figure 9. Py-GC-MS total ion current chromatograms. Forested LSP site 43: (A) whole soil, (B) Fraction 1 floated in DI water, (C) Fraction 2 floated in K1aq (1.6 g/mL), and (D) Fraction 3 sank in K1aq (1.6 g/mL). See Table 1 for peak identification.

(Two column)

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1459 320 A7] upon pyrolysis, accompanied by naphthalenes [N0-N2] with relatively minor phenols [F1-
1460 321 F3] and aliphatics [+] (Fig. 9D).
1463 322
1464 323 3.4.2. Barren site 25R soil
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1466 324 Site 25R is anomalously free of plant life (Fig. 4D), standing in stark contrast to its lushly
1469 325 vegetated surroundings (Fig. 4B, C). Haggmann et al. (2019) concluded that this is primarily due
1471 326 to the extraordinarily high heavy metal contamination of this narrow strip of land, formerly
1472 327 between train tracks (Fig. 2) which were removed when the railyard was closed in the 1960's
1473 328 (Gallagher et al., 2008a). The abundant coal particles in its soil are the subject of the present
1474 329 study.

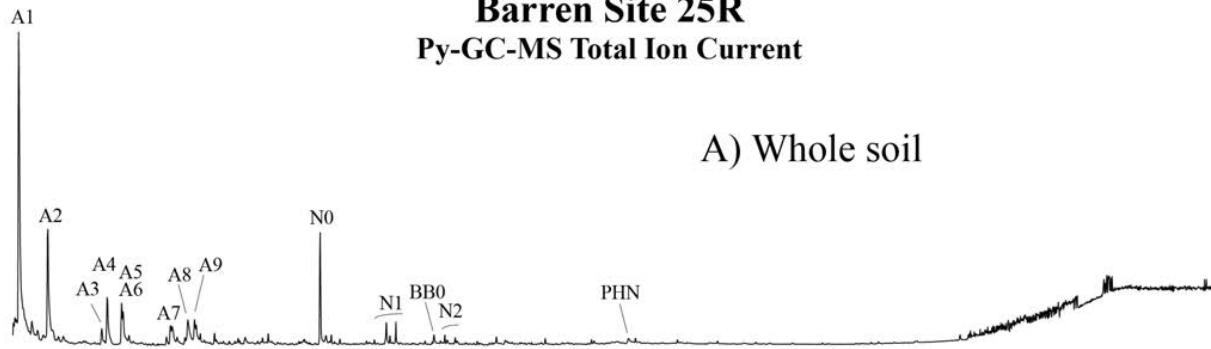
1480 330 Simple monoaromatic [A1-A9] and diaromatic [N0-N2, BB0] compounds with a trace of
1481 331 phenanthrene [PHN] comprise nearly all of site 25R's whole soil pyrolyzate (Fig. 10A). This
1482 332 site's < 2 mm soil size fraction previously pyrolyzed (Haggmann et al., 2019) yielded similar
1483 333 results but with a distinct shift towards the heavier aromatics. The first density fraction (Fig.
1484 334 10B) produced a contrastingly complex distribution of pyrolysis products, in particular,
1485 335 monoaromatics [A1-A5], polysaccharide and lignin markers [P1-P6, L1-L15], phenols [F1-F8],
1486 336 diketodipyrrole [DKDP], fatty acids [FA1-FA3], and steroids [S1-S3].

1495 337 Figure 10

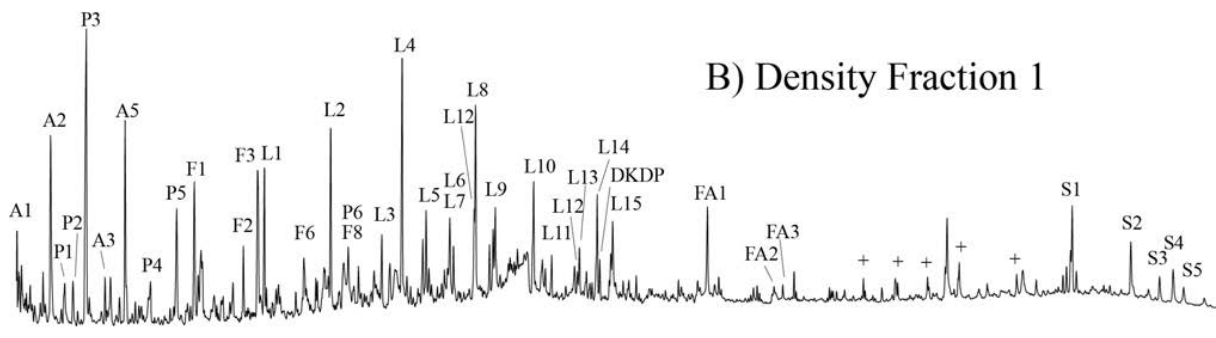
1496 338 The second density fraction's pyrogram is also complex, but it indicates a very different
1497 339 distribution of compounds (Fig. 10C). Monoaromatic [A1-A7] and diaromatic [N0-N3, BB1]
1500 340 hydrocarbons predominate, along with phenols [F1-F8]. Three to five-ring aromatic compounds
1501 341 are also in evidence, notably dibenzofurans [DBFx], phenanthrenes [PHNx], pyrenes [PYRx],
1502 342 chrysenes [CHRx], and benzo[e]pyrene [BeP]. Pristane [Pr] and *n*-alkanes [+] attest to a minor

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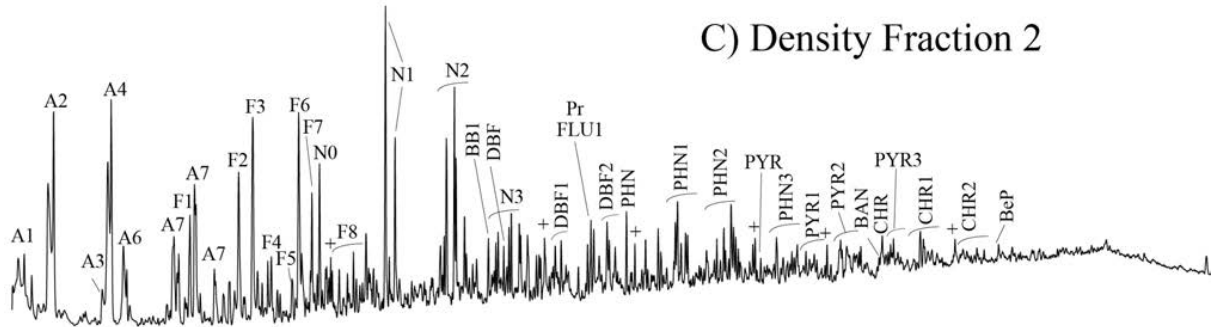
Barren Site 25R
Py-GC-MS Total Ion Current



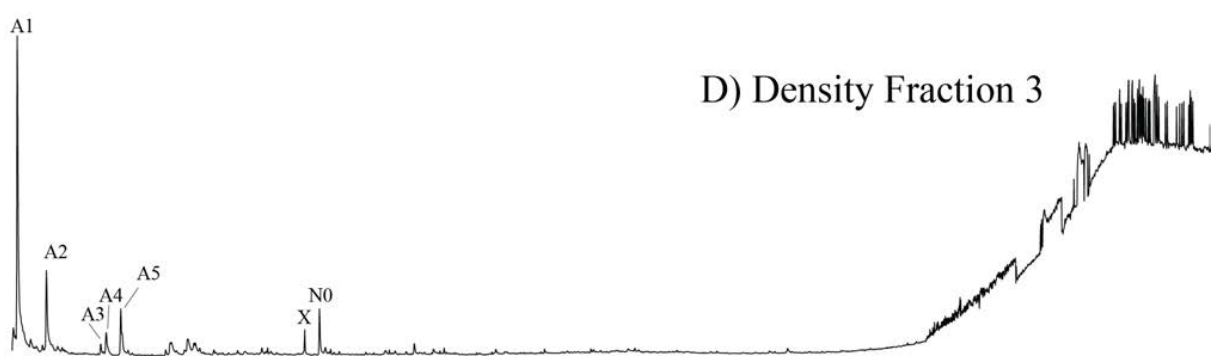
A) Whole soil



B) Density Fraction 1



C) Density Fraction 2



D) Density Fraction 3

Figure 10. Py-GC-MS total ion current chromatograms. Barren LSP site 25R: (A) whole soil, (B) Fraction 1 floated in DI water, (C) Fraction 2 floated in KIaq (1.6 g/mL), and (D) Fraction 3 sank in KIaq (1.6 g/mL). See Table 1 for peak identification.

(Two column)

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1571 343 aliphatic component. The third, residual density fraction offered a very limited yield upon
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1573 344 pyrolysis, mostly benzene [A1], a few other monoaromatics [A2-A5] and naphthalene [N0] (Fig.
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1575 345 10D).

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1580 347 3.4.3. Coal contamination in soil: Insights from Py-GC-MS of density fractions

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1582 348 A temperate forest soil is naturally rich in organic material, with roots, leaf litter, humus,
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1584 349 fungi, and soil microbes. Forested soils in LSP have an anomalously high organic matter
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1586 350 content: 30 % by weight in the case of site 43 compared to a natural background value of about
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1588 351 7.5 %, attributed to the additional burden of coal, coke and char contamination therein (Hagmann
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1590 352 et al., 2019). Pyrolysis of the whole soil should therefore yield a complex mixture of products
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1592 353 from all organic materials present, in proportion to the relative amounts of each type. Pyrolysis
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1594 354 proneness should also be considered as wood and coal would yield abundant pyrolysis products,
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1596 355 whereas coke and char would not. The combined effect can be seen in Figure 9A, showing
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1598 356 aromatic hydrocarbons together with polysaccharide and lignin marker compounds in site 43's
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1600 357 whole soil pyrolyzate.

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1602 358 The soil density fractionation experiment was undertaken in an attempt to separate the
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1604 359 soil's organic components to improve the specificity of the subsequent chemical analyses. A
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1606 360 critical factor was the isolation of the soil biomass from the fossil fuel contaminants present.
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1608 361 The pyrolysis products of the first density fractions of both soils (Figs. 9B, 10B) closely
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1610 362 resemble those of the soil vegetation detritus (Fig. 8A) in the predominance of lignin and
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1612 363 polysaccharide markers and steroids. Therefore, plant matter is evidently the main component of
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1614 364 the light fraction in both cases. The presence of diketodipyrrole [DKDP] – a known protein
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1616 365 pyrolysis product (Orsini et al., 2017) – and relatively more fatty acids in the density fractions is
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1627 366 most likely due to soil microbial contributions. Although site 25R is barren of plant life, trace
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1629 367 amounts of biomass were detected in its soil (Fig. 10B, Table 2), likely derived from the adjacent
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1631 368 vegetated areas (Fig. 4D).

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1634 369 The second density fractions (Fraction 2) of both soils also produced very similar
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1636 370 pyrolyzates (Figs. 9C, 10C). As described above, their pyrograms both show a predominance of
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1638 371 mono- and diaromatic hydrocarbons, and phenols, along with parent and alkylated PAHs. The
1639
1640 372 polysaccharide and lignin markers compounds characteristic of the vegetation debris are not
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1642 373 detected. These distributions in turn closely resemble those derived from the medium volatile
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1644 374 bituminous coal particle (Fig. 8C). It can be concluded that the second density fractions are
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1646 375 predominantly bituminous coal. The triterpenoids [BAM] evident in soil 43's pyrogram likely
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1648 376 indicate some, perhaps degraded, biomass contribution (Fig. 9C).

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1651 377 The third density fractions (Fraction 3) are alike in that their pyrolyzates contain
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1653 378 predominantly simple monoaromatic hydrocarbons (Figs. 9D, 10D). They bear a strong
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1655 379 resemblance to the anthracite pyrolysis products (Fig. 8B), indicating that anthracite is the
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1657 380 primary pyrolyzable component therein. The presence of anthracite in this residual density
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1659 381 fraction is likely due to the added mass of adhering mineral phases, as observed by SEM (Figs. 6,
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1661 382 7), precluding floatation in the 1.6 g/mL fluid employed. The site 43 pyrogram shows more of
1662
1663 383 the alkylbenzenes and naphthalenes, along with trace amounts of phenols, suggesting that some
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1665 384 bituminous coal is also present in this fraction, similarly burdened with mineral matter. The
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1667 385 minor C₁₁-C₂₆ *n*-alkanes detected (Fig. 9D) may arise from petroleum or coal tar-derived
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1669 386 contamination in the soil adhering to mineral phases. Solvent extraction to test this supposition
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1671 387 was beyond the scope of this project, but it is compatible with the conclusions of the prior study
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1673 388 which did employ extraction and subsequent GC-MS (Hagmann et al., 2019). This prior work
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1683 389 also documented the presence of coke and char in these soils, confirmed during the hand-picking
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1685 390 procedure of the present study (Sec. 2.3), but these materials yield little upon pyrolysis and thus
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1687 391 escape detection by Py-GC-MS.
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1691 393 4. Conclusions

1692
1693 394 Analytical pyrolysis provided compelling evidence for the presence of biomass and
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1695 395 bituminous and anthracite coal in the LSP soil density fractions. These insights should ideally be
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1697 396 checked by organic petrography. The simple density separation experiment undertaken in this
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1699 397 soil contamination study is shown to offer a helpful preparative technique, although not a
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1701 398 rigorously quantitative one. The procedure could be improved by a micronization pretreatment
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1703 399 step to more effectively permit separation of mineral components from the organic ones and by
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1705 400 organic petrographic confirmation of the fraction compositions.
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1707 401 Of primary concern with the presence of coal at Liberty State Park is the potential
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1709 402 environmental risk, principally due to coal's constituent PAHs. The abundant coal particles in
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1711 403 LSP soils are the legacy of the park's past as major rail yard and port for the large-scale
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1713 404 commercial transport and transfer of coal, powered by coal-fired steam locomotives, riding on
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1715 405 rails supported by wooden crossties likely treated with coal tar-derived creosote. However,
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1717 406 much of the LSP coal is anthracite and higher rank (medium volatile) bituminous. Extractable
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1719 407 PAH content in coal decreases markedly with increasing coal rank (Stout and Emsbo-Mattingly,
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1721 408 2008; Laumann et al., 2011), therefore high rank coal particles in soil should pose less of an
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1723 409 environmental concern on this basis. While the PAH-rich high volatile bituminous coal is
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1725 410 proportionately less abundant at LSP, the extent to which it might be toxic or mutagenic to
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1727 411 humans, plants, and animals is nonetheless linked to its degree of bioavailability. With the
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1739 412 evidently flourishing plant communities in great majority of the LSP brownfield zone, limited
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1741 413 hot spots of acute contamination therein (Hagmann et al., 2019) likely demand the most intensive
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1743 414 remediation efforts. Analysis of soil components by Py-GC-MS, particularly after a preparative
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1745 415 density separation procedure, is shown to be effective in the environmental forensic and
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1747 416 industrial archeological investigation of this urban brownfield. This detailed information about
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1749 417 the nature of contaminants will help to inform future remediation efforts in the public interest.
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1765
1766 425 memory of his longtime friend and colleague, the late Professor Jack Crelling, coal petrographer
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1768 426 and density separation pioneer.
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2100
2101 561 2158-2167.
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2103 562
2104
2105 563 Figure and table captions
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2107 564 Figure 1. Index map showing location of Liberty State Park (LSP) in Jersey City (NJ), USA, the
2108
2109 565 principal anthracite coal fields of Pennsylvania, and the former Central Railroad of New Jersey
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2111 566 main line. Base map: Google Earth; coalfields: Pennsylvania Dept. of Environmental Protection;
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2113 567 rail line: Anderson (1984).
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2115 568
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2117 569 Figure 2. The Central Railroad of New Jersey's rail yard and marine terminal in Jersey City as it
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2119 570 appeared in a 1954 aerial image, overprinted with the location of the two soil samples (25R, 43)
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2131 571 presented in this study. At the time of the photograph, coal transport operations were largely
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2133 572 confined to the zone seen in the lower part of the image, on the tracks leading to Pier 18. Note
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2135 573 the locations of the passenger terminal and roundhouse. Base image: U.S. Geological Survey;
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2137 574 identification of coal handling facilities: Anderson (1984); pier identification: Brooklyn
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2140 575 Historical Society Archives.

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2144 577 Figure 3. Historical images of CRRNJ coal transport operations in the 1940's. (A) Loaded coal
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2146 578 trains in Jim Thorpe, Pennsylvania (Fig. 1; town formerly known as Mauch Chunk). (B) Loaded
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2148 579 coal cars approach Pier 18 in the Jersey City rail yard. View to the west showing the yard's track
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2150 580 network (Fig. 2). (C) View of Pier 18's two coal dumping towers for transfer of coal from railcar
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2152 581 to barge. View is to the west from the eastern end of the pier. (D) View to the northeast of Pier
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2154 582 18's coal dumpers. Note Ellis Island in the background. Photos: Anderson (1984); used with
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2156 583 permission of the Delaware & Lehigh National Heritage Corridor, Inc., Easton (PA).

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2160 585 Figure 4. Appearance of Liberty State Park in 2017. (A) Aerial view towards the southwest
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2162 586 showing the study area within the park. Note the former passenger rail and ferry terminal,
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2164 587 partially restored but non-functioning, and the Liberty Science Center museum, built on the site
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2166 588 of the former railroad roundhouse (Fig. 2). Photo: D. Hagmann. (B, C) Dense vegetation covers
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2168 589 most of the study area. The top of the Liberty Science Center tower appears in C. (D) Soil
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2170 590 sample 25R was collected from this anomalously barren strip within the study area. Photos B-D:
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2172 591 M. Peters, Montclair State Univ.; used with permission.

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2187 593 Figure 5. Experimental flow chart. See section 2 for details. No vegetation detritus was picked
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2189 594 from site 25R soil. * < 2 mm size fraction previously studied in detail (Hagmann et al., 2019).
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2191 595
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2193 596 Figure 6. Scanning electron micrograph of fragments of a single wet-sieved (> 2 mm) and
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2195 597 sonicated LSP 43 coal particle. Note surface encrustations. Scale bar is 300 μm .
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2199 599 Figure 7. SEM EDS mapping images of a fragment of a single wet-sieved (>2 mm) and
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2201 600 sonicated LSP 43 coal particle. Scale bars are 50 μm . (A) SEM image; box shows element
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2203 601 mapping area for B-D. (B) Multi-element map (O, Fe, S, Cl, Si, Al) superimposed on SEM
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2205 602 image. (C) Element map for aluminum. (D) Element map for silicon. Element mapping images
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2207 603 indicate clay mineral platelets adhering to coal.
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2209 604
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2211 605 Figure 8. Py-GC-MS total ion current chromatograms of materials from the site 43 soil sample:
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2213 606 (A) typical soil organic matter (roots & twigs) and (B, C) two coal particles hand-picked from
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2215 607 the >2 mm size fraction after wet sieving and sonication. See Table 1 for peak identification.
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2217 608
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2219 609 Figure 9. Py-GC-MS total ion current chromatograms. Forested LSP site 43: (A) whole soil, (B)
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2221 610 Fraction 1 floated in DI water, (C) Fraction 2 floated in KI_{aq} (1.6 g/mL), and (D) Fraction 3 sank
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2223 611 in KI_{aq} (1.6 g/mL). See Table 1 for peak identification.
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2225 612
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2227 613 Figure 10. Py-GC-MS total ion current chromatograms. Barren LSP site 25R: (A) whole soil, (B)
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2229 614 Fraction 1 floated in DI water, (C) Fraction 2 floated in KI_{aq} (1.6 g/mL), and (D) Fraction 3 sank
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2231 615 in KI_{aq} (1.6 g/mL). See Table 1 for peak identification.
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617 Table 1. Pyrolysis-GC-MS peak identification for Figures 8-10.

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619 Table 2. Dry weight percentages of density fractions separated from whole soil of LSP Sites 43
620 and 25R. See text and Figure 5 for procedural details.