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An Organic Geochemical Assessment of CO₂-Coal Interactions During Sequestration

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An Organic Geochemical Assessment of CO₂-Coal Interactions During Sequestration

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ABSTRACT

Three well-characterized coal samples of varying rank were extracted with supercritical CO₂ to determine the amount of polycyclic aromatic hydrocarbons (PAHs) that could be mobilized during simulated CO₂ injection/sequestration in deep coal beds. The supercritical CO₂ extractions were conducted at 40°C and 100 bars, roughly corresponding to a depth of 1 km. The greatest amount of PAHs was extracted from the high-volatile C bituminous coal sample. Extracts from the subbituminous C and anthracite coal samples contained lower concentrations of these compounds. The effectiveness of supercritical CO₂ in liberating PAHs from the coal sample was evaluated in a comparison with a parallel series of Soxhlet extractions using 100% dichloromethane. More PAHs were extracted from the lower rank coal samples with dichloromethane than with supercritical CO₂. The results from this investigation indicate that, regardless of coal rank, CO₂ injection into deep coal beds may mobilize PAHs from the coal matrix. However, more PAHs could be mobilized during CO₂ sequestration in a high-volatile C bituminous coal bed than in either of the other two coal ranks studied.

INTRODUCTION

The marked increase in atmospheric levels of CO₂ resulting from anthropogenic activities has prompted concerns regarding the potential for global warming and climate change. Overall reduction of CO₂ emissions will likely involve some combination of mitigation techniques, but for the immediate future, sequestration of CO₂ in geological reservoirs (i.e., saline aquifers, depleted oil and gas reservoirs, and deep coal beds) seems especially promising, as experience from oil and gas production has already solved some of the technological obstacles (Bachu, 2001). Carbon dioxide sequestration in depleted oil reservoirs and deep coal beds has an advantage over disposal in saline aquifers by providing additional recovery of hydrocarbons (i.e., enhanced oil recovery [EOR] and enhanced coal bed methane [ECBM] recovery). The economic return provided by this additional hydrocarbon recovery could help offset the costs associated with CO₂ sequestration. The ultimate CO₂ storage capacities of deep coal beds are not well known, but estimates have indicated that up to hundreds of gigatons of CO₂ could be stored this geological reservoir (Gentzis, 2000; Herzog, 2001).

Although technologically feasible, CO₂ sequestration in deep coal beds is not without potential environmental consequences. For example, reservoir conditions in a number of coal-bearing basins are near or beyond the CO₂ critical point (Fig. 1). A current pilot study in the San Juan basin is injecting CO₂ into coal-bearing units as a supercritical fluid (Reeves and others, 2002). Supercritical CO₂ is a highly

effective solvent that is increasingly used in environmental studies to extract contaminants such as pesticides, polychlorinated biphenyls, and PAHs from geological matrices (e.g., Levy and others, 1994; Dean and others, 1996; Bjorklund and others, 1999). Thus, a potential, unintended result of CO₂ sequestration in deep coal beds is that toxic compounds such as PAHs could be extracted from the coal beds and adjacent strata. The successful implementation of this CO₂ sequestration approach therefore requires thorough characterization of not only the storage capacity of the coal beds, but also the chemical interactions between the injected CO₂ and subsurface hydrocarbons.

The objective of this study was to determine the amount of PAHs extracted from coal samples at pressure-temperature conditions commensurate with potential CO₂ injection scenarios. The coal samples used in this study were considered “well characterized” because companion measurements of proximate/ultimate analyses, petrography, and CO₂/CH₄ adsorption isotherms were available for each sample. The information gained from this study was used to evaluate the potential environmental consequences of CO₂ injection into deep coal beds.

METHODS

Coal Sample Preparation, Characterization, and Extraction

Three coal samples of varying rank were used in this study: a sample of subbituminous C coal from the Gulf Coast of Texas, a sample of high-volatile C bituminous coal from the Illinois basin, and a sample of anthracite coal from the Appalachian basin. The Gulf Coast coal sample was taken from a core section (Warwick and others, 2002) whereas the high-volatile C bituminous and anthracite coal samples were collected as channel samples. All three samples were sent to a commercial lab (Geochemical Testing; Somerset, PA) for grinding, sieving, and splitting. Petrographic, proximate, and ultimate analyses were performed on sample splits (Table I) to characterize each coal sample. Carbon dioxide and CH₄ adsorption isotherms were also measured on splits to determine the gas storage capacities for each coal sample (Gluskoter and others, 2002).

At the USGS, additional sample splits were taken and prepared for Soxhlet and supercritical fluid extractions. Prior to extraction, each coal sample was ground and sieved to isolate the 250-125 μm (60-120 mesh) fraction. The ground, sieved coal samples were rinsed three times with organic-free, deionized water to remove adhered fines, and then dried under air at 40°C in a gravity-convection oven. The 250-125 μm particle-size class was chosen to maximize the ability of dichloromethane, used in the Soxhlet extractions, to extract hydrocarbons from the coal matrix while avoiding the effects of coal agglomeration that are frequently encountered at finer particle sizes (Azzam and others, 1992). This additional sieving, although necessary, may have induced sample fractionation such that the final 250-125 μm samples were no longer representative of the original coal samples. Additional proximate/ultimate analyses are currently underway to ascertain the extent of fractionation that may have taken place.

Portions of the 250-125 μm coal samples were extracted using supercritical CO₂ at 40°C and 100 bars. These pressure-temperature conditions were selected to simulate CO₂ sequestration scenarios in coal beds at a depth of 1 km. The extractions were conducted using an ISCO SFX 220 extraction unit coupled to two ISCO 260D syringe pumps; 100% “SFE-grade” CO₂ was used in the extractions. For each extraction, approximately one gram of the 250-125 μm coal sample was weighed into a 10 ml-capacity extraction vessel and spiked with 10 μl of a surrogate solution containing four perdeuterated PAHs. The supercritical fluid extraction program consisted of a 15-minute static (no-flow) step followed by a 45-minute dynamic (flow) step at a flow rate of approximately 1.8 ml min⁻¹. The extracted hydrocarbons were collected in a solvent trap containing chilled (0°C) hexane. Method blanks, consisting of baked quartz sand, were processed with every batch of samples to monitor for contamination.

A parallel series of extractions were conducted using 100% dichloromethane (DCM) in a Soxhlet apparatus. This procedure approximated the total extractable organic matter (EOM) procedure used in petroleum geochemistry to characterize source rocks (Hunt, 1996), and thus provided a frame of reference from which to evaluate the effectiveness of supercritical CO₂ in extracting hydrocarbons from coal samples. In the Soxhlet extraction procedure, five grams of a ground coal sample were weighed out into a 25 ml-capacity glass extraction thimble, spiked with 10 µl of the PAH surrogate solution, and extracted for 24 h. Both the Soxhlet and supercritical fluid extraction procedures were designed such that comparable solvent:coal ratios were used in each procedure. The supercritical fluid extractions used approximately 1.6 moles of CO₂ to extract one gram of coal sample, whereas the Soxhlet extractions used approximately 1.7 moles of DCM to extract each gram of coal sample. Considering that the boiling point of DCM at atmospheric pressure is 40°C, both types of extractions were also conducted at essentially the same temperature.

Both the Soxhlet and supercritical fluid extracts were concentrated under a gentle stream of nitrogen to a volume of 5 ml. At this point, 100 µl of the extract was removed to determine the extractable organic matter (EOM) content. After the EOM determination, the Soxhlet extracts were further evaporated to <100 µl, and the extracts were diluted with hexane to precipitate asphaltenes. The hexane-diluted extracts were centrifuged when necessary to facilitate separation of the asphaltene and maltene fractions.

Sample Fractionation

The sample extracts were separated into three compound classes using preparative chromatography. Sample columns (11-mm i.d.) were packed in DCM with 1 ml activated copper, 2.5 g neutral alumina (5% water-deactivated), 2.5 g silica 62 (100% activated) and 5.0 g silica 923 (100% activated). The solvent was switched to hexane, and then the column was charged with the sample extracts. The aliphatic, aromatic, and polar fractions were consecutively eluted from each column using 100% hexane, a 30:70 (v/v) DCM:hexane mixture, and 100% methanol, respectively. The aromatic fraction was subsequently evaporated under a gentle stream of nitrogen to a final volume of 2 ml. Fractionated extracts were stored at 4°C until analysis.

Gas Chromatography-Mass Spectrometry Analyses

Polycyclic aromatic hydrocarbon concentrations in the aromatic fractions of the sample extracts were quantitated using an Agilent 6890 Gas Chromatograph (GC) interfaced with an Agilent 5973 Mass Selective Detector (MSD). The MSD was operated in the selective ion monitoring (SIM) mode during the PAH analyses. External PAH standards were run with each batch of samples to generate five-point concentration-response curves. All samples and external standards were spiked with 10 µl of an internal standard solution containing 4,000 ng µl⁻¹ of each of six perdeuterated PAHs. Samples were injected in the splitless mode, and the temperature program was optimized (Table II) to maximize resolution of the compounds of interest. The target analytes consisted of 30 PAHs and included both parent compounds and alkylated homologs (Table III), such as naphthalene (C₀) and the homologs methyl-naphthalene (C₁), dimethyl-naphthalene (C₂), and trimethyl-naphthalene (C₃).

RESULTS

Supercritical CO₂ Extractions

The supercritical fluid extracts from the high-volatile C bituminous coal sample contained the greatest total concentration of the 30 target PAHs. However, all three coal sample extracts yielded quantifiable levels of PAHs (Fig. 2). The total extractable PAH concentrations are expressed on a per gram dry coal basis, and have not been corrected for variations in ash content or fixed carbon content. Alkylated naphthalenes (C₂ and C₃) and phenanthrenes (C₀ - C₂) dominated the extract from the high-volatile C bituminous coal sample. The C₀- and C₁-naphthalenes were detected in the sample extract, but at levels below the limits of quantitation. None of the target PAHs beyond chrysene was detected. Conversely, the extract of the subbituminous C coal sample was dominated by the higher molecular weight PAHs, e.g., benzo[b]fluoranthene, benzo[a]pyrene, and indeno[1,2,3-cd]pyrene, and contained very low levels of compounds in the naphthalene and phenanthrene homologous series. The anthracite sample extract contained trace amounts of alkylated naphthalenes and phenanthrenes; no other target PAHs were detected.

The high-volatile C bituminous coal extract contained target PAHs at concentrations approximately two to four times greater than those determined in the other sample extracts. However, examination of the total MSD response obtained during the SIM-mode analysis readily shows that, in addition to the target compounds, many more PAHs were extracted from the high-volatile C bituminous coal sample than from the other two samples (Fig. 3). In addition to the target compound responses, there are several unidentified peaks with molecular masses corresponding to 156 or 170 mass units, likely indicating the presence of additional isomers of dimethylnaphthalene and trimethylnaphthalene.

Soxhlet-DCM Extractions

The aromatic fraction of the Soxhlet-DCM extract obtained from the high-volatile C bituminous coal sample contained detectable levels of all target PAHs. The four most abundant compounds in the Soxhlet extract from this sample were 1-methylphenanthrene, phenanthrene, 2,3,5-trimethylnaphthalene and chrysene. Lesser amounts of the sulfur-containing compounds, benzothiophene and dibenzothiophene, were recovered. The Soxhlet extract also contained appreciable amounts of the higher molecular weight PAHs, e.g., benzo[a]pyrene, that were not detected in the corresponding supercritical CO₂ extract. The anthracite coal sample extract contained very low levels of PAHs; a number of the target compounds were present at levels below limits of quantitation and only the high molecular weight compounds, e.g., benzo[a]pyrene, indeno[1,2,3-cd]pyrene, and dibenz[a,h]anthracene, were detected at appreciable levels. The subbituminous C coal sample extract consisted mostly of high- to medium-molecular weight aromatic compounds. Compounds with molecular weights less than C₃-naphthalene were present at relatively low concentrations in the subbituminous C coal extract.

The total amount of target PAHs extracted using the Soxhlet-DCM procedure varied with coal rank in a manner similar to that observed for the supercritical CO₂ extracts. The high-volatile C bituminous coal sample yielded the greatest PAH concentrations on a per gram dried coal basis, followed by the subbituminous coal sample and then the anthracite coal sample (Fig. 4). Both extraction procedures yielded comparable total PAH concentrations for the subbituminous C coal and anthracite coal samples. However, PAH concentrations in the supercritical CO₂ extract from the high-volatile C bituminous coal sample were much lower (~ 7%) relative to those measured in the corresponding Soxhlet extract.

DISCUSSION

Ability of Supercritical CO₂ to Extract Polycyclic Aromatic Hydrocarbons from Coal Samples

The ability of supercritical CO₂ to extract PAHs from the coal matrix was evaluated using the PAH yield of Soxhlet-DCM extractions as a baseline for comparison. Dichloromethane-based extractions have been typically used to determine the total extractable organic matter content associated with source rocks (Hunt, 1996). Although suitable for source rocks, dichloromethane may not be as effective at extracting hydrocarbons from coal samples. Dichloromethane may only extract hydrocarbons from the outermost surface of the coal particles (Wender and others, 1981). Despite this possible limitation, the prevalent usage of DCM and related chlorinated hydrocarbons, e.g., chloroform, (Brooks and Smith, 1967; Boudou, 1984; Hopfgartner and others, 1990; Radke and others, 1990) to extract hydrocarbons from coal renders this procedure a suitable frame of reference for evaluating supercritical CO₂ extractions.

The PAH extraction efficiencies of DCM and supercritical CO₂ were comparable for the subbituminous C and anthracite coal samples. However, the low PAH yield of the supercritical CO₂ extract from the high-volatile C bituminous coal sample relative to the corresponding DCM extract seems somewhat counterintuitive. Bituminous coal beds have typically experienced pressure-temperature conditions during burial to reach the oil-generation window. As a result, bituminous coals tend to contain free hydrocarbons, including PAHs, that were produced by thermal cracking reactions and then subsequently trapped within the coal porosity network (Durand and others, 1977; Monthieux and Landais, 1987; Radke and others, 1990). Supercritical CO₂ should readily extract these “free” hydrocarbons from the coal matrix, because supercritical CO₂ can dissolve appreciable amounts of PAHs. For example, using published solubility measurements involving individual PAHs in supercritical CO₂ (e.g., McHugh and Paulaitis, 1980; Johnston and others, 1982; Zerda and others, 1986), one would predict that as much as an order of magnitude more PAHs should have been extracted from the high-volatile C bituminous coal sample. The individual PAH solubility measurements notwithstanding, the observed low PAH yields may have resulted from an association between PAHs and asphaltenes within the coal porosity network. Asphaltenes are polar, high molecular weight compounds that are only slightly soluble in supercritical CO₂ (Guiliano and others, 2000). If the PAHs liberated during the DCM extractions were largely associated with asphaltenes in the high volatile C bituminous coal sample, then the supercritical CO₂ may not have been sufficiently polar to disrupt these associations, resulting in the diminished extraction efficiency. Extractions involving supercritical CO₂ modified with a polar cosolvent could be used to test this hypothesis.

Ramifications for CO₂ Sequestration in Deep Coal Beds

Supercritical CO₂ has been shown to extract PAHs from three coal samples of varying rank. Mobilization of PAHs from the coal sample matrix has some ramifications for CO₂ sequestration in deep coal beds. For example, migration of CO₂ away from the sequestration site and out of the coal seam could transport PAHs and other hydrocarbons into adjacent subsurface environments. In addition, supercritical CO₂ has been shown to effectively extract hydrocarbons from sedimentary rocks (Monin and others, 1988). Thus, CO₂ migrating out of coal beds could also extract additional organic compounds from adjacent strata.

The supercritical CO₂ extraction conditions used in this study, 40°C and 100 bars, were mild enough that there was no accompanying chemical degradation of the coal matrix. Such mild extraction conditions constitute a “nonspecific extraction” (Wender and others, 1981), whereby hydrocarbon extraction involves the diffusion of hydrocarbons through the coal matrix followed by dissolution into the extracting medium. In this study, the extracting medium was a supercritical fluid, and previous studies

with supercritical fluids have shown that diffusion-limited extraction effects, i.e., related to the particle size, are not present at particle sizes less than approximately 1-2 mm diameter (Maddocks and others, 1979). Diffusion-limited extraction effects, however, will likely be more important at larger scales, i.e., core sections of coal or entire coal beds. As a result, the combined use of ground coal samples and relatively short-duration extractions in this study may not be representative of PAH extraction and transport during CO₂ sequestration in deep coal beds, particularly at prolonged injection times.

One additional aspect of CO₂ sequestration in coal beds concerns the role of water in the mobilization of hydrocarbons during CO₂ injection. For example, prolonged injection of CO₂ at supercritical conditions may require disposal of produced water because supercritical CO₂ is highly effective at displacing water from the coal matrix (Iwai and others, 1998). Concurrent displacement of water and PAHs from the coal matrix may degrade the quality of the produced water such that special disposal measures would be necessary. The work presented here specifically did not include water to reduce the number of variables potentially affecting extractable PAH yields. Future work will include water, either as equilibrium moisture associated with the ground coal samples or using water-modified CO₂ as the extracting fluid, to investigate the influence of water on the mobilization and transport of PAHs within coal beds.

CONCLUSIONS

Supercritical CO₂ at 40°C and 100 bars was found to extract the greatest amount of PAHs from a high-volatile C bituminous coal sample, and lesser amounts of PAHs from subbituminous C and anthracite coal samples. The supercritical CO₂ extracts from the subbituminous C and anthracite coal samples contained PAH concentrations comparable to those in the corresponding Soxhlet-dichloromethane extracts, indicating similar extraction efficiencies for the two solvents. The supercritical CO₂ extract from the high-volatile C bituminous coal sample contained significantly fewer PAHs than the companion Soxhlet-DCM extract. Despite variations in extraction efficiency, the extraction results demonstrated that PAHs may be mobilized from coal beds during carbon dioxide sequestration/injection and could possibly affect water quality in the vicinity of the injection site.

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DISCLAIMER

Any use of trade, product, or firm names in this report is for descriptive purposes only and does not imply endorsement by the U.S. Government.

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Table I. Proximate/ultimate analyses and petrographic analyses for the coal samples used in this study.

Sample Name	PA-2-CN2	20011006 A3	PAS-1224
Location	Gulf Coast	Illinois basin	Appalachian basin
Coal Rank	subbituminous C	high volatile C bituminous	anthracite

Proximate, as-received basis

Btu/lb	8006	11916	12052
Ash %	11.11	5.52	10.16
Moisture %	30.87	11.78	7.98
Sulfur %	0.53	0.62	0.94
Fixed Carbon	29.44	45.79	75.11
Btu/lb, MMMF	9098	12684	13563
Fixed Carbon, DMMF	51.65	55.79	93.09

Ultimate, as-received basis

Hydrogen %	6.43	x	2.75
Carbon %	46.59	x	75.36
Nitrogen %	1.04	x	0.71
Sulfur %	0.53	x	0.94
Oxygen %	37.73	x	10.08
Ash %	11.11	x	10.16
Free Swelling Index	0	x	0
Apparent Specific Gravity (g cm ⁻³)	1.37	x	1.53

Petrography
Maceral Content

Vitrinite (%)	53.6	91	83
Liptinite (%)	8.8	4.4	0
Inertinite (%)	36.4	4.4	7
Ro (%)	0.45	0.59	4.14

MMMF: moist, mineral-matter free

DMMF: dry, mineral-matter free

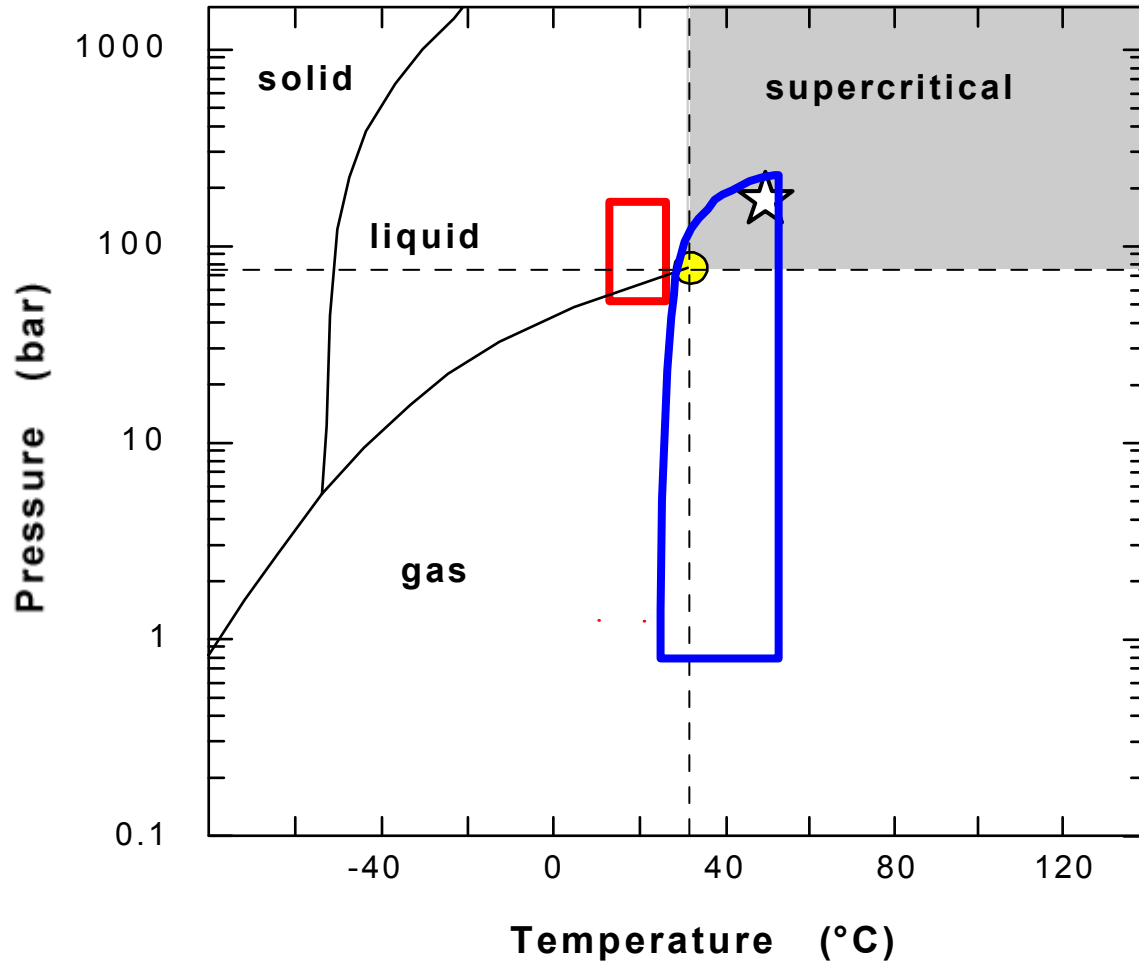
x: analyses pending

Table II. Gas Chromatography-Mass Spectrometry Conditions for Quantitative PAH Analyses.

Parameter	Setting
Injector Temp	280°C; splitless mode
Injection Volume	1 μ L
Carrier Gas / Flow Rate	He; 0.9 ml min ⁻¹
Initial Oven Temp	50°C, hold 4.0 min
Oven Program	10°C min ⁻¹ to 150°C; 6°C min ⁻¹ to 230°C; 3°C min ⁻¹ to 300°C; 10°C min ⁻¹ to 310°C, hold 5 min
Column	HP5-MS; 30m x 0.25mm x 0.25 μ m

Table III. Target Compounds for Quantitative Analyses.

Analyte	Formula Weight (g mol ⁻¹)
naphthalene	128
1-benzothiophene	134
1-methylnaphthalene	142
2-methylnaphthalene	142
biphenyl	154
1-ethylnaphthalene	156
2-ethylnaphthalene	156
2,6-dimethylnaphthalene	156
acenaphthylene	152
1,2-dimethylnaphthalene	156
acenaphthene	153
2,3,5-trimethylnaphthalene	170
fluorene	166
dibenzothiophene	184
phenanthrene	178
anthracene	178
1-methylphenanthrene	192
3,6-dimethylphenanthrene	206
fluoranthene	202
pyrene	202
benz[a]anthracene	228
chrysene	228
benzo[b]fluoranthene	252
benzo[k]fluoranthene	252
benzo[e]pyrene	252
benzo[a]pyrene	252
perylene	252
indeno[1,2,3-cd]pyrene	276
dibenz[a,h]anthracene	278
benzo[ghi]perylene	276



- CO₂ critical point
- Powder River Basin (*estimated*)
- ⏏ Black Warrior basin (*Pashin and others, 2002*)
- ★ CO₂ injection conditions, San Juan basin (*Reeves and others, 2002*)

Figure 1. Comparison between CO₂ phase behavior and known/estimated pressure-temperature conditions within coal-bearing basins.

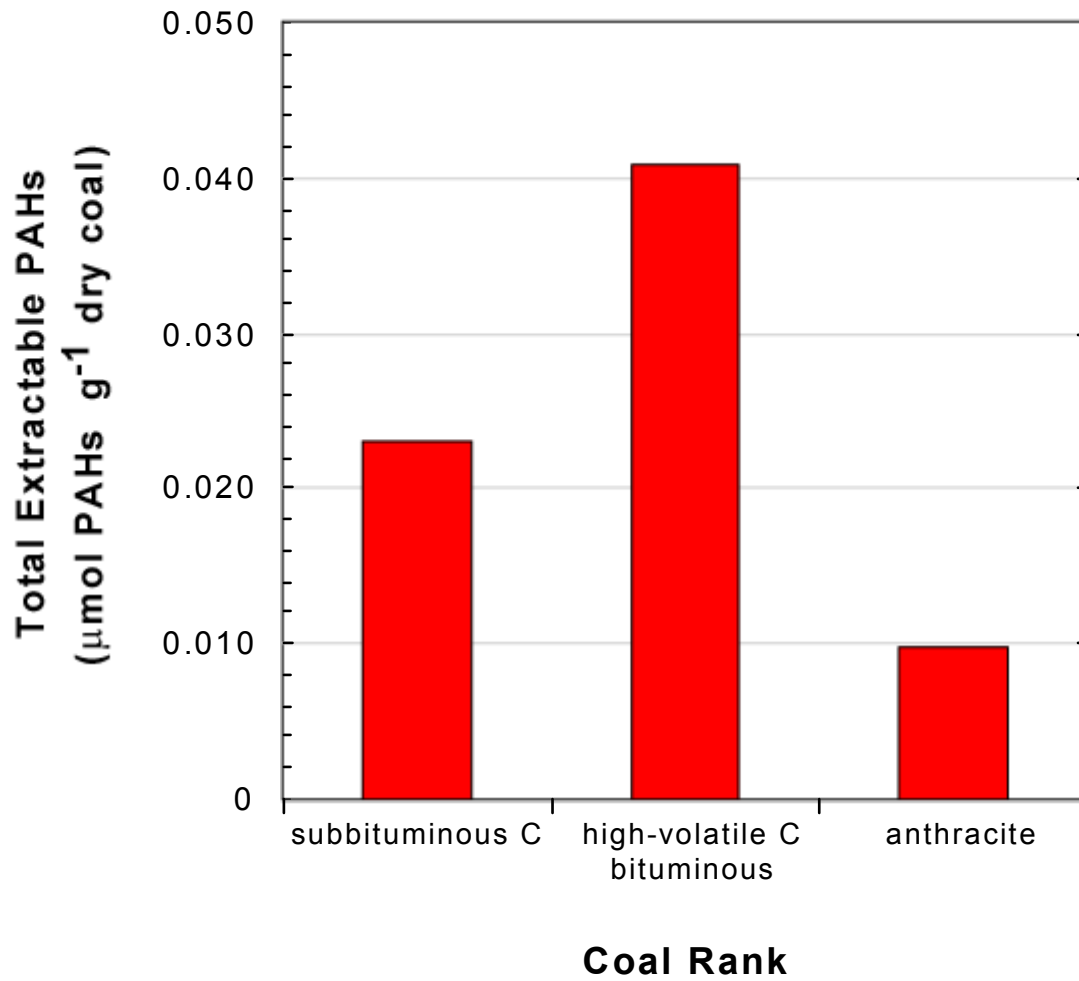


Figure 2. Effect of coal rank on total PAHs extracted with supercritical CO₂.

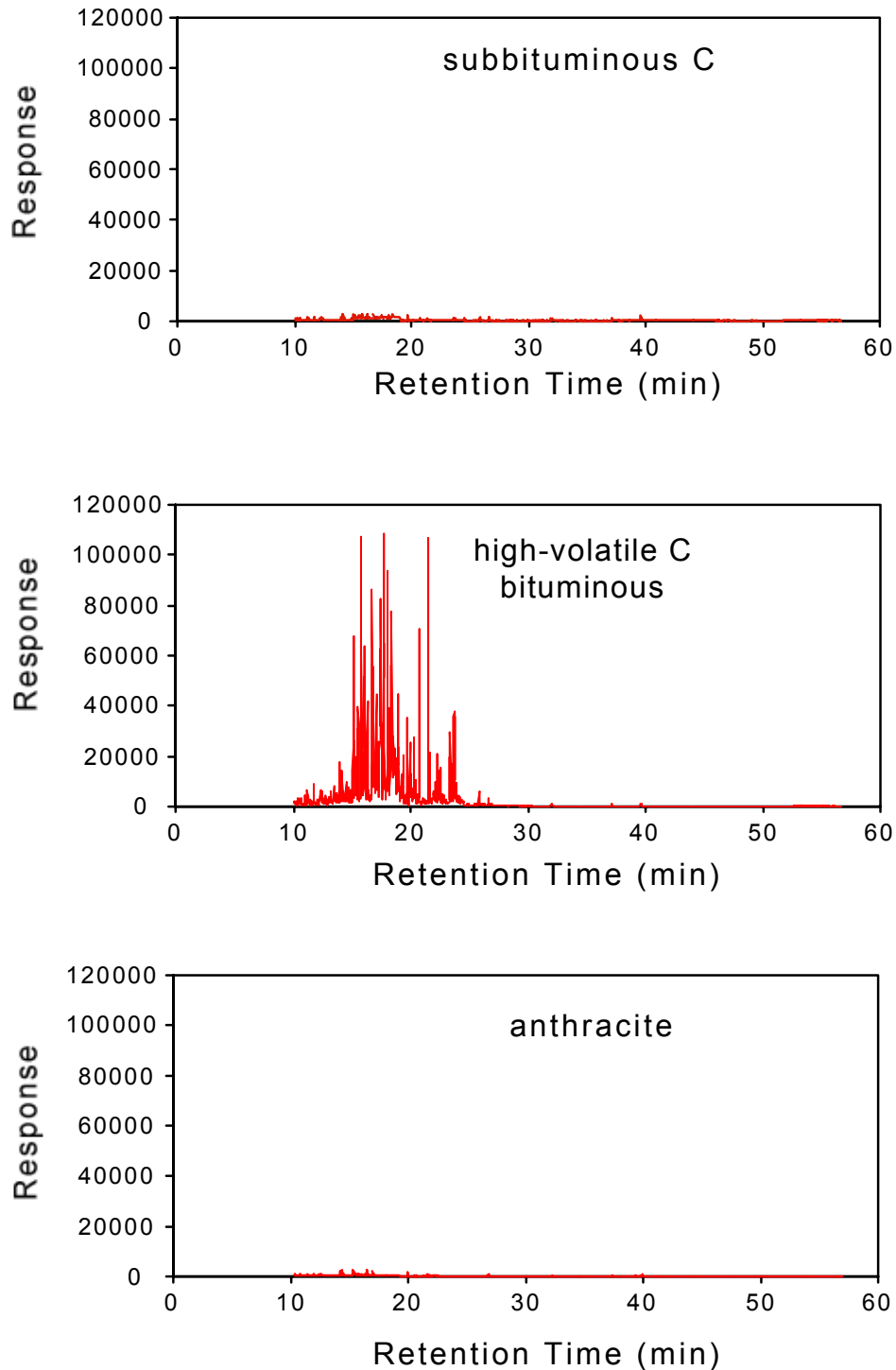


Figure 3. Extracted ion (EI) chromatogram depicting the collective response of all target PAH compounds. (An EI chromatogram represents a portion of the total detector response during an analysis. The responses due to internal standards and surrogate compounds have been subtracted from the total response to emphasize responses of the target PAH compounds. Note that all EI chromatograms have been scaled to same response levels to facilitate direct comparison.)

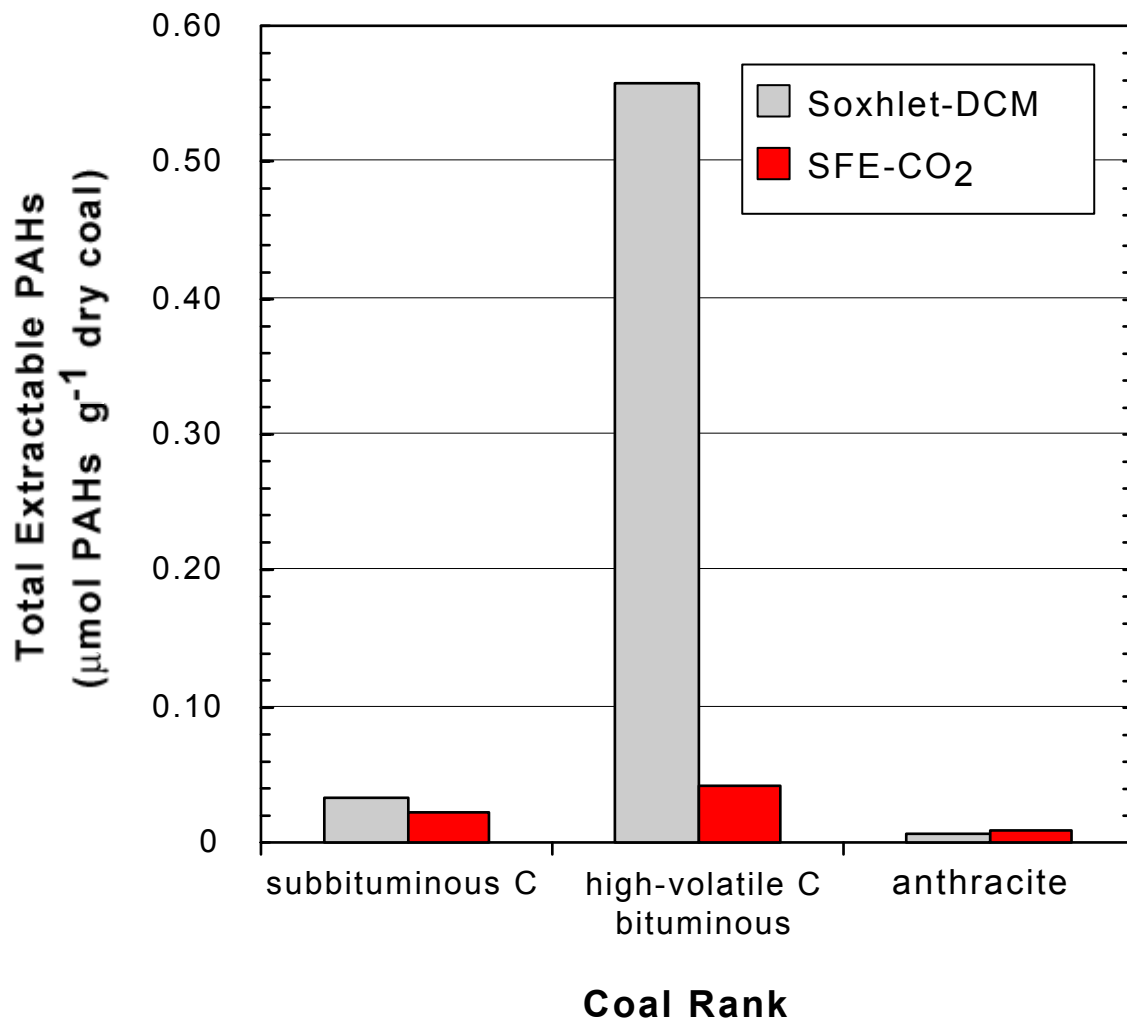


Figure 4. Comparison between total PAH yields obtained during supercritical CO₂ extractions and Soxhlet-DCM extractions.