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THE SUPERCRITICAL FLUID EXTRACTION OF ANTHRACENE AND PYRENE FROM A MODEL SOIL : AN EQUILIBRIUM STUDY

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ABSTRACT

Supercritical carbon dioxide (SC-CO_2) is used to extract two polycyclic aromatic hydrocarbons (PAHs), anthracene and pyrene, from a model soil at conditions ranging from 35 to 55 °C and 7.79 to 24.13 MPa. Equilibrium partition coefficients and Freundlich isotherm constants are determined for the two PAHs on white quartz sand and the model soil. The effect on equilibrium of additional water in the soil phase is also examined.

INTRODUCTION

One group of sites (>2000) that requires remediation are the old town-gas manufacturing facilities, which produced liquid coal tar as a byproduct. Coal tar is laced with PAHs and some of these organics are known to be carcinogenic. These old facilities disposed of the coal tar by pouring it into open surface pits. The liquid tar then sorbed into the soil, saturating it with PAHs.

The traditional methods of incineration, land filling, or liquid extraction to destroy or remove PAHs from soils and other porous materials are not considered either environmentally acceptable or economical. Biodegradation of the contaminant organics by microbes is applicable; however, the process is slow. The biodegradation appears limited by the physical desorption of the contaminants from the soil to the microbial aqueous phase, not by the degradative process of the microbes (1). Heavy organic compounds (non-volatile and hydrophobic, such as PAHs) desorb naturally at very slow rates and may migrate deep within a soil particle over time, thus limiting their bioavailability to the microbes. The PAH desorption process could be enhanced by using a supercritical fluid to remove the contaminant(s) from the soil.

Supercritical fluid extraction (SCFE) offers distinct advantages over conventional liquid extraction for the removal of organics from soils. Due to their low surface tensions (2), supercritical fluids (SCF) can easily penetrate porous materials such as soils. Their liquid-like densities allow for good solubility of organic compounds. SCFs cleanly dissolve and precipitate solutes with the added ability to vary their solving power with small changes in temperature and pressure (2). Compared to liquids, SCF's have enhanced mass transfer characteristics due to low viscosities, high diffusivites, and large buoyant effects caused by large interfacial density gradients (2).

Carbon dioxide (CO_2) has a critical temperature of 304.1 K, a temperature well within ambient conditions. This property allows the extraction process to be carried out at temperatures not likely to destroy thermally labile compounds. The critical pressure of 7.38 MPa (1070.3 psia) is easily reached and exceeded in the laboratory, and industry. CO_2 is also non-toxic, non-flammable, and is commercially abundant. These factors make CO_2 the SCF solvent of choice for these experiments and other applications such as the removal of other PAHs, PCBs, DDT, and hexachlorobenzene from soils and other types of environmental solids (3,4,5,6,7,8).

Adsorption isotherms for anthracene and pyrene on soil in contact with supercritical carbon dioxide have been determined and modeled. Phase distribution coefficients have also been determined for the PAHs on soil as well as white quartz sand. This equilibrium data should help the engineer better understand the effects of temperature and pressure on equilibria involved with SC-CO_2 and soil systems. This knowledge, in turn, will assist in better design of supercritical fluid extraction processes.

EXPERIMENTAL

Figure 1 shows a schematic of the experimental apparatus used in these experiments. It is similar in design to that used by Tan et al. (9). The apparatus is unique however in that both mass transfer and equilibrium data can be taken on this dynamic packed bed extractor system. The apparatus is versatile enough to accommodate temperatures ranging from ambient to 373 K and pressures from ambient to 68.95 MPa. The capability to add entrainers to enhance extraction is also present.

Liquid solvent, CO_2, flows from an inverted tank into an ice bath to prevent vaporization due to ambient heating. It is then fed into a LDC/Milton Roy dual head, mini metering pump (Model # 2396-89). The pump is a positive displacement, reciprocating plunger type. The dual pump heads have brass heat exchangers installed on their exposed faces to prevent unsteady pump operation, i.e., decreasing efficiency. The exchangers remove the heat generated by friction and compression of the CO_2 as the pump piston moves forward, preventing the vaporization of the liquid CO_2. This, in turn, allows correct control and metering of the liquid flow rate.

The pressurized solvent is then fed into a surge tank located in a second isothermal bath maintained at the extraction temperature. The internal volume of the surge tank is approximately 500 cm^3, and its purpose is to damp out the pressure pulses in the system caused by the pump. This allows for smooth, piston like flow through the extractor.

The solvent leaves the surge tank and enters a thermal equilibrium coil, then enters the bottom of a stainless steel mixing vessel also located in the same bath. This vessel is filled with pure PAH or 3 mm diameter glass beads coated with a co-solvent depending upon the experiment undertaken. The isothermal bath is maintained at the experimental temperature with a Haake E3 Immersion Circulator with a temperature control accuracy of ±0.02°C.

The solvent then enters the vertical extraction cell also in the bath. The cell is 15 cm in length and 1.3 cm in diameter and filled with approximately 20 cm^3 ($\approx$ 26.5 grams) of contaminated soil. The ends of the cell are capped by a layer of porous metal (10μm) to detrain any soil particles from the SCF stream. The cell is not tightly packed to avoid pressure drop effects. It is packed uniformly to avoid dead spaces, or "short circuiting" of

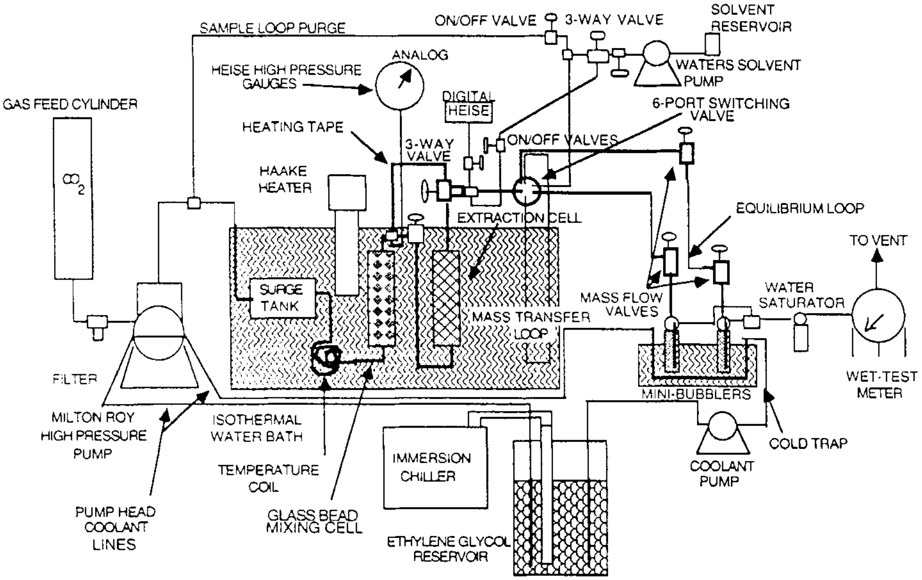


FIGURE 1. SUPERCRITICAL FLUID EXTRACTION APPARATUS

the solvent. The uniformity of the packing also creates plug or piston like flow to assure equilibrium between the solutes and solvent.

Once the fluid leaves the extractor, it enters a six-port sampling valve (Rheodyne Co., 7010) which can be switched to isolate the two loops in which samples are collected. Flow through the loops and thus the extractor is controlled with Autoclave micro-metering mass flow valves. The two sample loops are located after the high pressure micro-metering valve and the six-port switching valve (note Figure 1). The loop after the mass flow valve is used to collect a cumulative sample for the phase partition study. The other loop is used to collect mass transfer samples. A Waters Associates Liquid Chromatography Pump (M#6000A) is used to flush both loops with a liquid solvent (methylene chloride). Mini-bubblers are placed at the ends of the sample loops to detrain and collect the precipitated solute.

Both loops are then vented through a H_2O gas saturator and a calibrated wet-test meter with a stated accuracy of ±0.5% of volume through the meter. The wet-test meter is used to measure the total volume of CO_2 that had passed through the extractor. A second isothermal cold bath using chilled ethylene glycol is used as a cold trap for the mini-bubblers and the equilibrium sample loop.

The system pressure is measured by a HEISE Digital Indicator with a range of 0 - 41.37 MPa (0 - 6000 psia) connected to the extraction cell. The gauge is reported to have an accuracy of ±0.01% of full scale, and was calibrated by Heise at the factory using a dead weight pressure tester.

The temperatures of the baths are measured with Platinum Resistant Thermometers (PRT) connected to a Keithley 135A Digital Multimeter. The PRTs were calibrated with a National Bureau of Standards certified platinum resistance thermometer. Temperature can be measured to a ±0.04°C accuracy.

Model Sand/Soil Description and Preparation

Sand and a model soil are used as the solid phase matrix for these experiments. The white quartz sand has a -50 +70 mesh size. The uncontaminated model soil is 66.2% sand and 33.8% silt/clay with 3% organic carbon and 0.79% water. Galbraith Laboratories of Knoxville, TN did the analytical combustion analysis for the organic carbon and percent water determinations. Sieves # 35, 120, and 200 were used to classify the soils into 0.11, 0.03 and, 0.01cm average diameter particles.

The model soil is spiked with a PAH by dissolving a known amount of the PAH solute in 10ml of methylene chloride. This is then pipetted onto the amount of soil required to fill the reactor volume, mixed well, and allowed to stand overnight at room temperature, in a hood, to allow the solvent to evaporate.

Experimental Procedure

Prior to any experimental run, the entire system is purged with CO_2 at the current tank pressure. Both the mixing and extraction cells are cleaned with acetone and then air dried prior to each experiment. The cells are then packed with PAH or soil as determined by the experiment being conducted and installed back into the system. The isothermal bath is then filled with distilled water and the immersion circulator activated.

The isothermal bath is allowed to reach a steady temperature. The valve on the CO_2 tank is opened slowly to allow flow upstream into the inlet of the Milton Roy pump. Once the pressure reaches 5.86 MPa (850 psig), the Milton Roy pump is activated to begin compression of the liquid CO_2 to the desired extraction pressure. Once pressurization is complete, the fluid stream is allowed to flow through the system for 30 minutes to achieve steady state using the extractor by-pass. The system is now ready for the adsorption or extraction sampling procedures to begin.

The pure PAH and SC-CO_2 equilibrium studies are conducted first. Two plugs of pure PAH, approximately 2.5 g each (≈ 5 g total), are evenly packed in the mixing cell. The effluent concentration is then measured over time until a steady value is reached, approximately 30 mins. The system temperature and/or pressure are then changed and the experiment repeated until the isotherms are completed. Prior to the pure PAH/SC-CO_2 experiments, a study was conducted to determine if position of the PAH plugs within the mixing cell affected equilibrium. From this data , it was concluded that position did not affect equilibrium.

For the soil adsorption studies, pure PAH is left in the mixing cell while clean soil is placed in the extraction cell. CO_2 is allowed to flow through the mixing cell until it becomes saturated and the effluent concentration reaches a steady state. The saturated SCF stream is then diverted through the soil in the extraction cell. Again, effluent concentration is measured until it returns to the initial value. The soil is then removed from the extraction cell and weighed to obtain the amount of material adsorbed. Soxhlet extraction of the soil is also performed to confirm the amount of material adsorbed.

Desorption studies are conducted by first lab-spiking the soil to a concentration of 500 ppm with the PAH. The soil is then packed into the extraction cell. The pure PAH is of course removed from the mixing cell and after being thoroughly cleaned installed back in the system. The extraction process is allowed to continue for 30 minutes at steady flow. The extracted PAH is deposited on the inner surface of the equilibrium loop after precipitating from the flashing CO_2. After which, the equilibrium loop is flushed with solvent and collected in the bubbler. The sample is removed from the bubbler and the bubbler washed. The sample is then allowed to evaporate in a hood, mixed with toluene, and then analyzed using the GC.

The soil is then removed form the extraction cell and placed within a Soxhlet extractor. Methylene chloride is used to extract the remaining PAH for approximately 8 hours. This sample can then be removed and analyzed on the GC. The Soxhlet extraction allowes a check on material balances by determining the amount of remaining PAH on the soil. The material balances could be closed to within 15%.

The sand experiments are conducted in the same manner.

RESULTS AND DISCUSSION

Figure 2 shows the experimental results, with mean and standard deviation, of tests conducted to assure that equilibrium was not being affected by increases in the superficial velocity through the extractor. Statistically, the equilibrium mole fraction did not appear to be affected by a three orders of magnitude increase in the superficial velocity. This data validates the assumption of equilibrium assumed in the bed at low pump settings, i.e., superficial velocities.

Figures 3 and 4 compare the pure PAH and SC-CO_2 equilibrium for anthracene and pyrene to literature data at 308, 318, and 328 °C. The data is plotted showing the equilibrium mole fraction of the PAH in the dense phase versus system pressure. The experimental data follows the literature data closely considering that most of the literature data was obtained by static or batch methods. Note that no literature data could be found for pyrene at 45 and 55 °C. The previous data confirms the capability of the dynamic packed bed system to determine equilibrium data for porous materials contacted with SC-CO_2.

The equilibrium phase partition coefficient, K_D, is a fundamental parameter of interest for the extraction of pollutants from soils because it determines the extent to which the extraction may be carried out. The parameter is defined as the ratio of the weight fraction of contaminant in the supercritical dense phase to the weight fraction of contaminant in the soil and water phases at equilibrium.

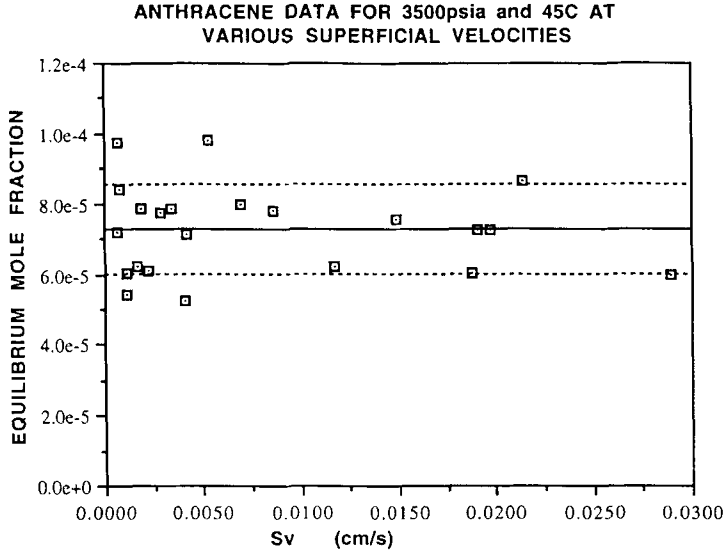


FIGURE 2. EFFECT OF SUPERFICIAL VELOCITY ON EQUILIBRIUM MOLE FRACTION

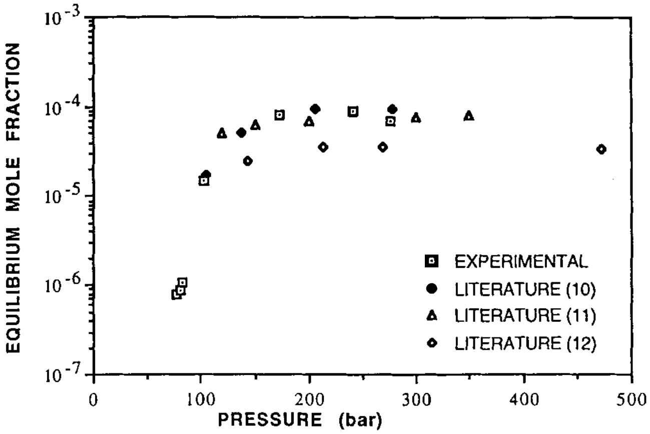
Figures 5 and 6 show the phase partition coefficients as functions of temperature and SC-CO_2 density for both the sand and model soil systems. K_D increases with increasing temperature and density. Anthracene and pyrene for both the sand and soil systems have K_Ds of approximately the same magnitude. Greater retention of both PAHs is observed for the soil phase, i.e., greater SC-CO_2 density is required to remove the PAHs. This is to be expected since the sand has no carbon sites for adsorption; only surface removal is seen.

The soil adsorption isotherms are modeled based on the Freundlich isotherm (14) :

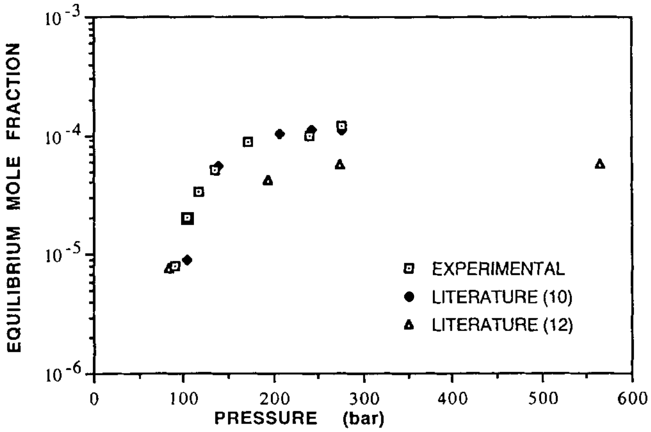
$$Q = Kf\, C^{1/n} \qquad (1)$$

where Q is the equilibrium adsorption capacity for the solid phase (g solute/g soil), C is the equilibrium concentration for the SCF dense phase (g solute/cm^3 SC-CO_2), and Kf and n

ANTHRACENE EXPERIMENTAL AND LITERATURE COMPARISON AT 35C



ANTHRACENE EXPERIMENTAL AND LITERATURE COMPARISON AT 45C



ANTHRACENE EXPERIMENTAL AND LITERATURE COMPARISON AT 55C

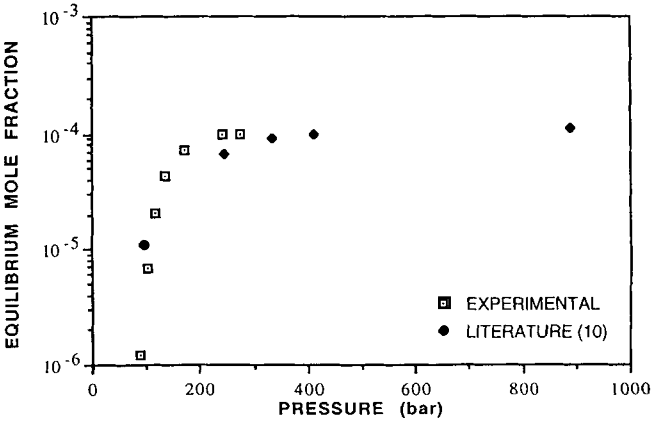


FIGURE 3. PURE ANTHRACENE EXPERIMENTAL AND LITERATURE SCF EQUILIBRIUM MOLE FRACTION COMPARISON

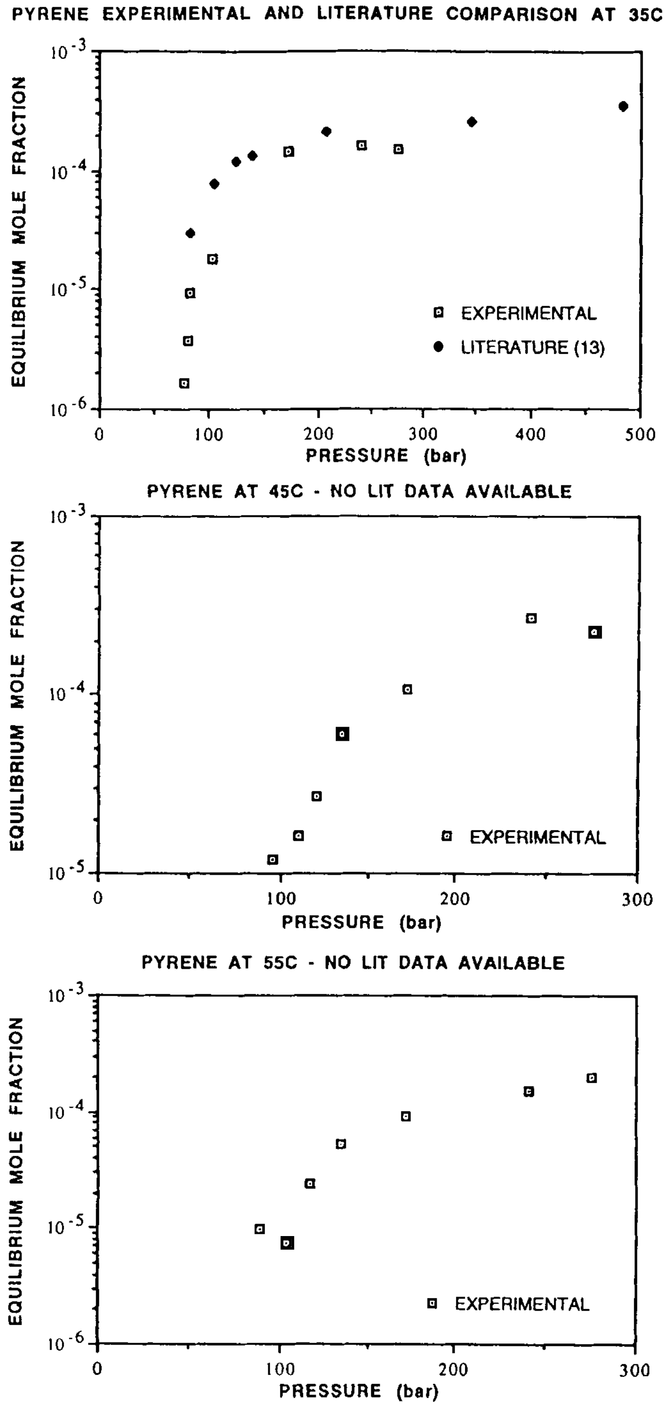


FIGURE 4. PURE PYRENE EXPERIMENTAL AND LITERATURE SCF EQUILIBRIUM MOLE FRACTION COMPARISON

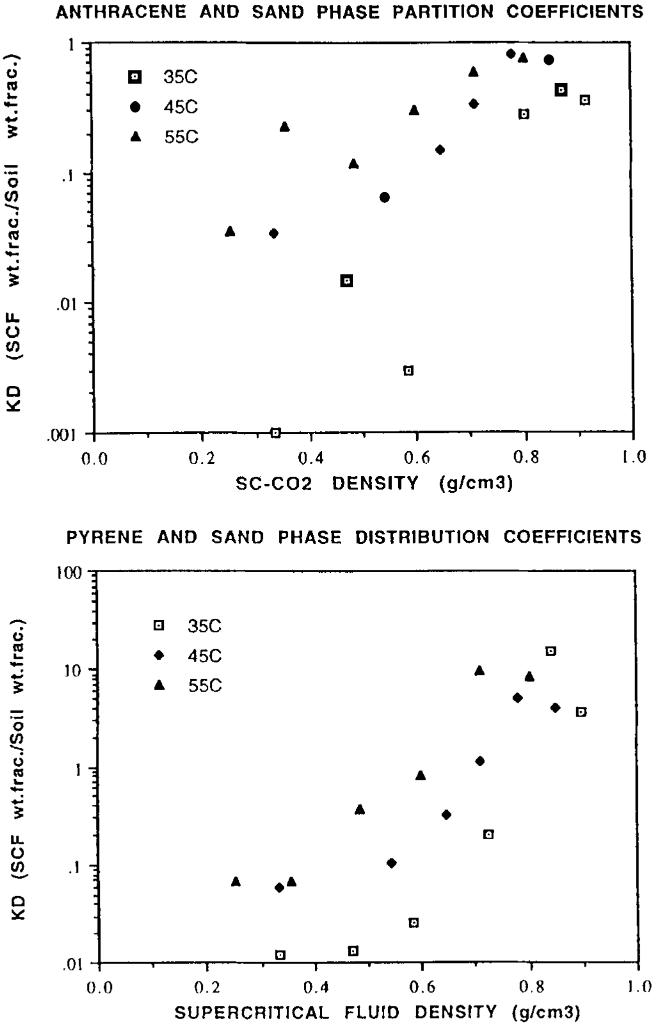
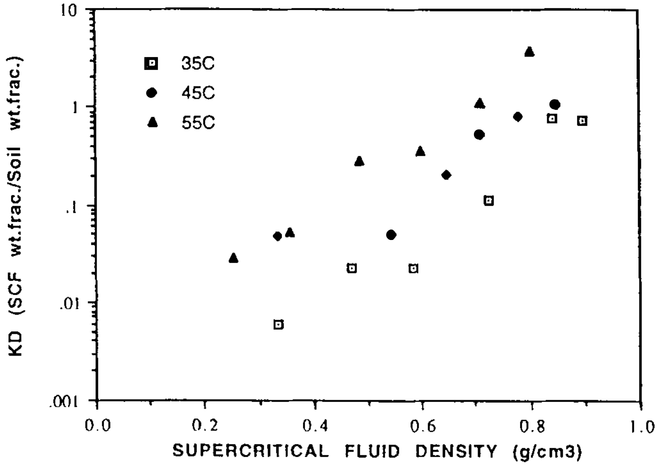


FIGURE 5. SAND/SC-CO_2 PHASE PARTITION COEFFICIENTS

ANTHRACENE AND SOIL PHASE PARTITION COEFFICIENTS



PYRENE AND SOIL PHASE PARTITION COEFFICIENTS

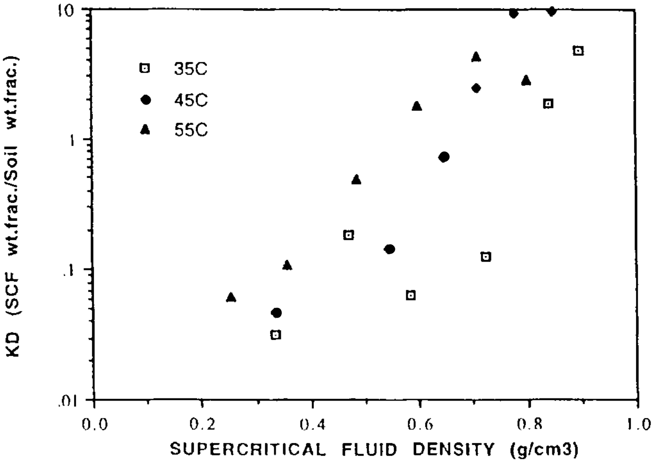
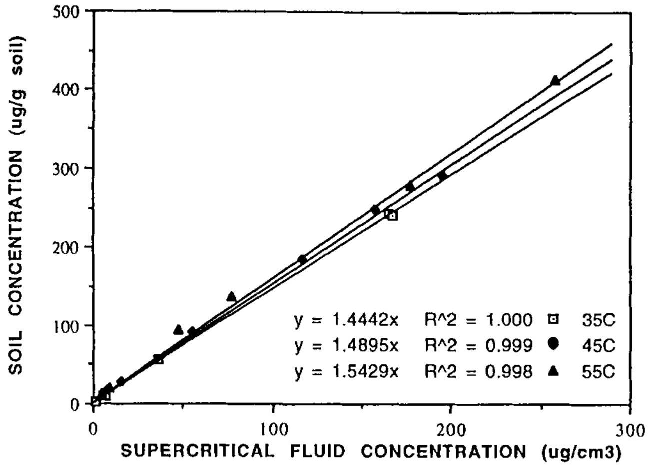


FIGURE 6. SOIL/SC-CO_2 PHASE PARTITION COEFFICIENTS

ANTHRACENE/SOIL ISOTHERMS



PYRENE/SOIL ISOTHERMS

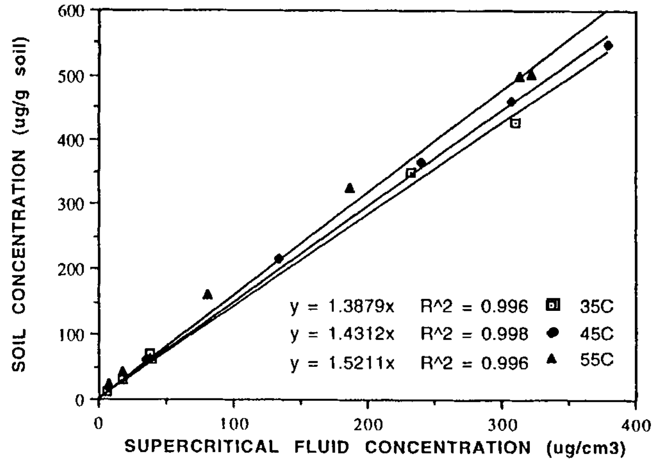


FIGURE 7. PAH SOIL ADSORPTION ISOTHERMS

TABLE 1. FREUNDLICH CONSTANTS FOR ANTHRACENE AND PYRENE ON A MODEL SOIL

SOLUTE	TEMP (K)	Kf	1/n
ANTHRACENE	308	1.44±0.4	1
	318	1.49±0.5	1
	328	1.54±0.6	1
PYRENE	308	1.39±0.5	1
	318	1.43±0.4	1
	328	1.52±0.5	1

are constants representing solid sorptive capacity and affinity of adsorbent for adsorbate respectively.

Figure 7 shows plots of the isotherms for anthracene and pyrene on the model soil with best fit model equations, where R^2 is the correlation coefficient. The data are linear requiring1/n = 1. Table 1 gives the Freundlich constants for the two systems. Kf increases with temperature indicating soil uptake increases with temperature. This occurs despite a decrease in SCF concentration resulting from decreased solubility. Pyrene uptake in soil is slightly greater than for anthracene indicating a preference of the soil for the more polar compound.

Figures 8 and 9 represent equilibrium mole fractions of the different systems : pure PAH, sand, and soil at all three temperatures. The anthracene/soil system at 35 °C exhibits an unusual situation. The soil isotherm lies above (greater SCF concentration) the pure anthracene and sand isotherms. This indicates that the soil "pushes" the anthracene out into the dense phase in greater concentration than pure anthracene would. This isotherm has been repeated several times with the same result being obtained. The pyrene data follows a more expected course. Both the pyrene and anthracene isotherms come together with an increase in temperature indicating the decrease in solubility in the dense phase and an increase in uptake in the solid phase.

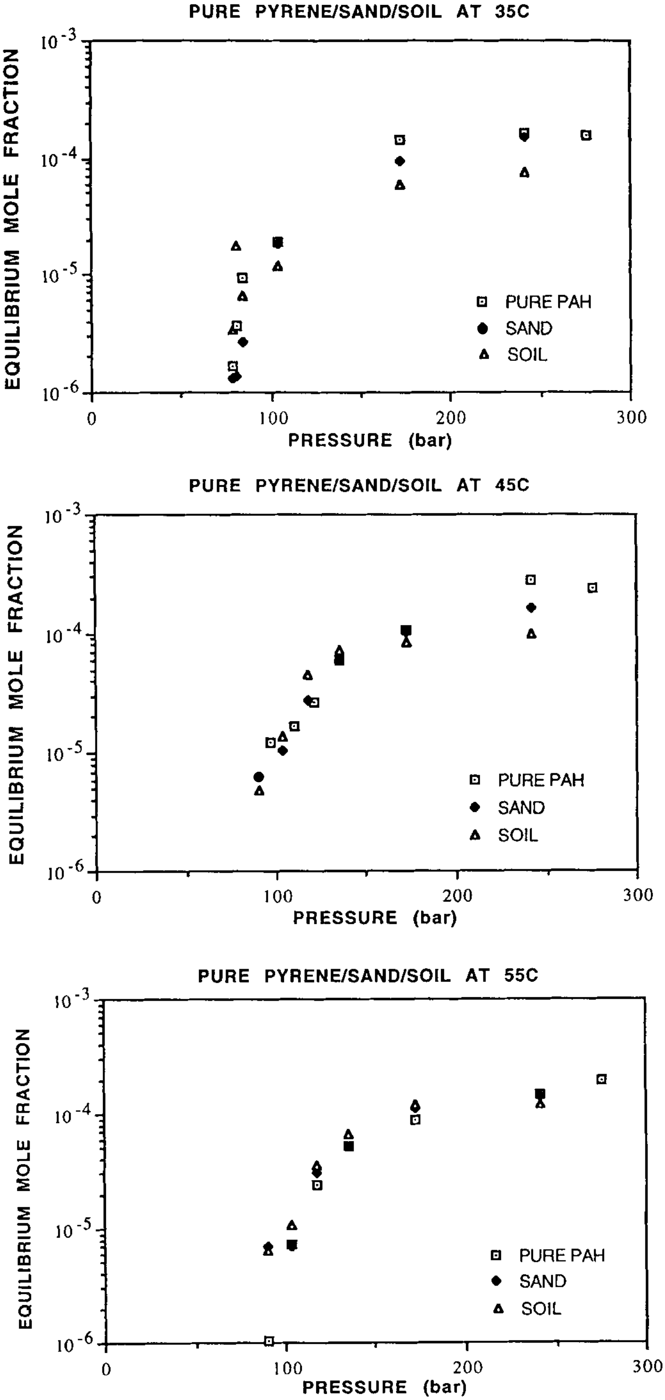


FIGURE 9. PYRENE SCF EQUILIBRIUM MOLE FRACTION COMPARISON OF PURE PAH, SAND, AND SOIL SYSTEMS

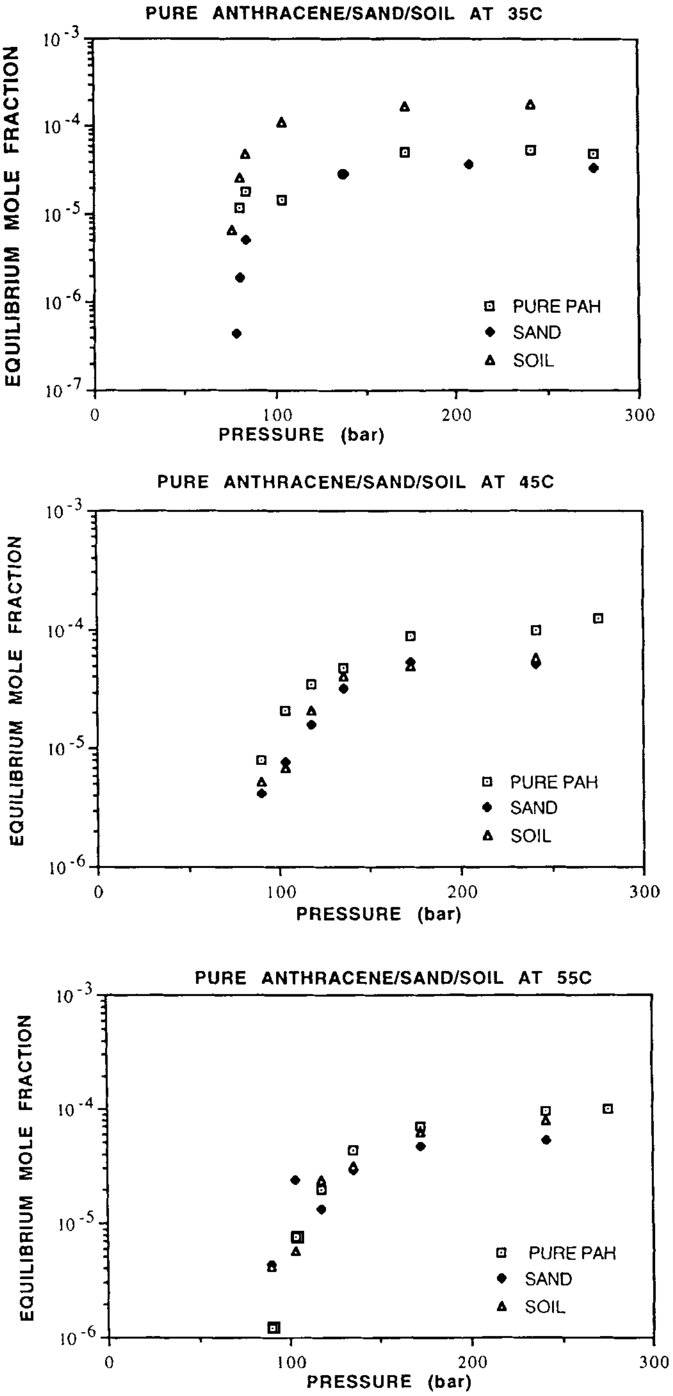
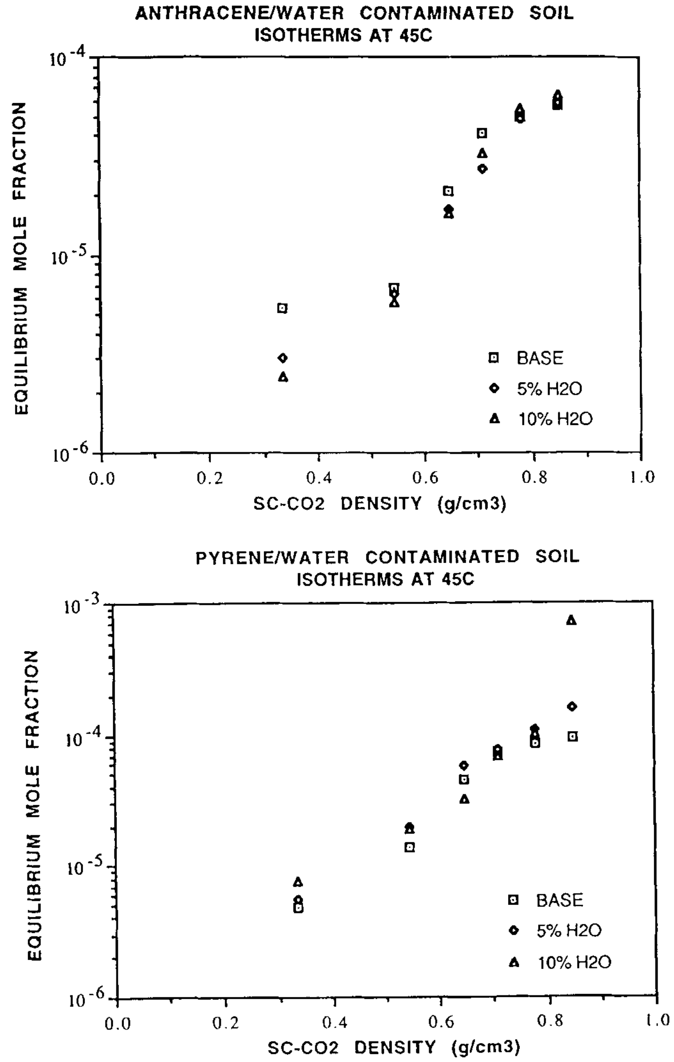


FIGURE 8. ANTHRACENE SCF EQUILIBRIUM MOLE FRACTION COMPARISON OF PURE PAH, SAND, AND SOIL SYSTEMS



ANTHRACENE/WATER CONTAMINATED SOIL ISOTHERMS AT 45C

PYRENE/WATER CONTAMINATED SOIL ISOTHERMS AT 45C

FIGURE 10. PAH SCF EQUILIBRIUM MOLE FRACTION COMPARISON OF BASE, 5%, AND10% ADDED WATER FOR SOIL SYSTEM

The addition of water to the soil in 5 and 10 wt.% amounts was done to determine the effect of water in the solid phase on the extraction process. Figure 10 shows 45°C isotherms for anthracene and pyrene. The data are scattered; however, the trends show an increase in the dense phase equilibrium mole fraction with increasing SC-CO_2. There also appears to be no statistical difference among the isotherms at the varying moisture contents. This lack of difference may be due to the narrow moisture content range used, as well as, the large experimental error involved obtaining the data . Expected results should show an increase in the mole fraction of PAH in the dense phase with increasing moisture content.

CONCLUSIONS

Adsorption isotherms for anthracene and pyrene on soil contacted with supercritical carbon dioxide are measured and modeled with the Freundlich isotherm on a linear basis. The equilibrium phase partition coefficients ranged from 0.03 to >9. The coefficients became greater than 1.0, which indicates enhanced solubility in the SCF phase, at reduced pressures greater than 1.2. The use of sand as a porous adsorbent showed no great affect upon phase distribution. Pyrene shows a greater phase partitioning between soil and SC-CO_2 than anthracene, possibly due to it's greater acentric factor (dipole moment). The addition of water to the soil phase, up to 10 weight percent above base weight, showed no statistical difference in the isotherms for the cases studied. Increasing the moisture content may help improve the data.

Future work will entail a mass transfer study to develop a radial penetration model to adequately describe desorption of PAHs from soils. The study will determine the effective intraparticle diffusivity, and overall mass transfer coefficient.

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