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Equilibrium Partitioning of Polycyclic Aromatic Hydrocarbons from Coal Tar into Water

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■ Partitioning of several polycyclic aromatic hydrocarbons (PAHs) from eight coal tar samples into water was measured. The measured partition coefficients were used to evaluate a model derived using Raoult's law convention for activity coefficients and hypothetical supercooled liquid solubilities. Our analysis suggests that the extent of deviations from "ideal" behavior for coal tar-water partitioning is sufficiently small, similar to earlier reports for gasoline-water and diesel-water partitioning of PAHs. The concentrations of PAHs in groundwater in equilibrium with these complex wastes, estimated from the model presented, may be considered as a reasonable approximation for most field-scale applications. The likely reasons for deviations from the ideal behavior are discussed, as are sources of analytical and computational errors.

Introduction

In the late 1800s and early 1900s, gas was manufactured from coal and oil for residential, commercial, and industrial uses. Manufactured gas plants (MGPs) were present in most major cities throughout the United States. The gas manufacturing plants generated a variety of process wastes such as tars, spent oxides, ash, sludge, ammonia liquors, and lampblack. The wastes generated from various methods of gas production were similar; however, the specific type and quantity of waste contamination at a given MGP site would be dependent on the feedstock used, the manufacturing process employed, and the time period over which the plant was in operation. In many cases, the wastes were left on-site in pits or containers, placed in nearby ponds or lagoons, or taken to off-site areas for land disposal. Such practices resulted in contamination of soils and groundwater at most former MGP sites.

Coal tars make up a large portion of the hydrocarbon wastes generated at MGP sites. Eng and Menzies (1) reported that more than 11 billion gallons of coal tar was generated in the United States during the period 1816-1947, but the disposition of several billion gallons is unknown and remains unaccounted. Coal tars are complex mixtures of a large number of hydrocarbons spanning a broad spectrum of molecular weights, with the concentrations of individual constituents varying significantly from one MGP site to another. The coal tar constituents of specific interest in this study are the polycyclic aromatic hydrocarbons (PAHs). These compounds have been detected at former MGP sites and are of particular concern

due to their potential carcinogenic nature (2). Several of these compounds have already been included on the U.S. EPA list of priority pollutants.

Near the source of contamination (presence of separate organic phase) at a coal tar disposal site, one of the primary processes controlling the release of organic chemicals is solubility. In the past, it has often been assumed that organic contaminant concentrations in the aqueous phase leaving a coal tar source would be equal to their corresponding pure compound aqueous solubilities. This may be a reasonable estimate if the source of interest was composed of a single contaminant; however, most complex wastes (e.g., coal tar, diesel, and gasoline) consist of mixtures of contaminants. These mixtures may be considered complex on the basis of the number of chemicals that constitute the mixture. On the other hand, complexity of a mixture can be defined by considering how the properties of the mixture deviate from some "ideal" behavior, regardless of the number of components. The former view corresponds to a mixture being *complex in composition*, whereas the latter implies *complexity in behavior*. The important point is that a mixture can be complex in composition without being complex in behavior and vice versa.

The properties of an organic mixture complex only in composition are determined by the properties of its pure components and their concentrations in the mixture. This implies that the chemicals of interest behave ideally in the matrix containing them. Under these conditions, the concentration of a chemical in the aqueous phase is proportional to the mole fraction of the chemical in the organic phase corresponding to Raoult's law. With the stated assumptions, the concentrations of a chemical in the aqueous phase in contact with a complex mixture can be predicted using the following simplified expression based on Raoult's law (3, 4):

$$C_w = x_o S_1 \quad (1)$$

where C_w is the chemical's concentration in the aqueous phase (mol/L) in equilibrium with the organic phase, S_1 is the aqueous solubility of the pure liquid chemical (mol/L), and x_o is the mole fraction of the chemical in the organic phase. For compounds that are solid in their standard state, the hypothetical supercooled liquid solubility (S_1) should be used (3). The applicability of Raoult's law has been shown for several mixtures of organic chemicals, including gasoline (4) and diesel fuel (3), for predicting aqueous-phase concentrations.

Table I. Selected Physicochemical Properties for the PAHs Investigated

compound	mp ^a (°C)	MW ^a	S _w ^b (mg/L)	log S ^d
naphthalene	80.2	128.2	32	-3.05
1-methylnaphthalene	-22	142.2	27 ^a	-3.72 ^e
2-methylnaphthalene	34	142.2	26 ^c	-3.62
acenaphthylene	82	152.2	3.93	-4.02
acenaphthene	93	154.2	3.42	-3.98
fluorene	116.5	166.2	1.9	-4.03
phenanthrene	100	178.2	1.0	-4.5
anthracene	216.3	178.2	0.07	-4.49
fluoranthene	107	202	0.27	-5.19
pyrene	150	202	0.16	-4.85
chrysene	254	228.2	0.006	-5.29
benz[a]anthracene	156	228.2	0.0057	-6.29
benzo[a]pyrene	179	252	0.0038	-6.28

^a Verschueren (14). ^b Crystal solubility at 25 °C (15) unless stated otherwise. ^c Miller et al. (16). ^d Supercooled liquid solubility calculated by assuming a constant ΔS_f for PAHs (3). ^e Liquid solute at standard state.

In order to assess the extent of groundwater contamination and the long-term environmental impacts from land disposal at former MGP sites, it is necessary to characterize the total amounts and the release rates of PAHs from the waste matrix. In addition, predictions of the patterns of mobilization and dissipation of PAHs in soils and groundwater must be investigated. This study focuses on the first aspect and will be limited to the use of equilibrium theory; however, rate-limited mass-transfer processes will also be important.

Materials and Methods

Chemicals. For all the PAHs investigated (See Table I), standards were purchased from Aldrich Chemical Co. at >98% purity except for acenaphthene, which was available only at 85% purity. Methylene chloride, the solvent used for the aqueous-phase extractions, was purchased from Fisher Scientific at Fisher grade Optima.

Batch Equilibration Technique. Approximately 0.3–0.5 g of coal tar was added to a glass centrifuge tube (nominal volume 40 mL), enough electrolyte solution (0.01 N CaCl₂) was added such that no headspace remained, and tubes were closed with phenolic caps fitted with Teflon-lined septa. Prior to sampling the coal tar for equilibration with an aqueous phase, coal tars were rotated end-over-end at room temperature (23 ± 2 °C) for 12–18 h. The coal tar–water (0.01 N CaCl₂) mixtures were then equilibrated for 3–7 days in the dark. Preliminary studies where samples were equilibrated for 1, 3, 5, and 7 days showed no measurable differences in PAH concentrations after 3 days. Following centrifugation (300 RCF for 30 min) of the equilibrated coal tar–water mixtures, a portion of the aqueous phase (≈25 mL) was quantitatively removed for extraction with methylene chloride and subsequent concentration prior to analysis. The compounds of interest were present in sufficiently large quantities such that experimental artifacts from PAH sorption to the equilibration vessels were considered negligible. To avoid volatilization losses and contamination of the aqueous-phase aliquot with the coal tar phase, the aqueous aliquot was removed through the septum using a 50-mL Teflon-backed gas-liquid syringe equipped with a 3-in. needle. The equilibration vessel was vented during sampling by piercing the septum with a second needle.

Following aqueous-phase transfers, as much residual water as possible was removed from the equilibration vessel without loss of the coal tar. The coal tar in the equi-

Table II. Range of Properties Observed for Eight Coal Tars (5)

physical properties	range	elemental anal.	range
ash (%)	0–50	carbon (%)	43–90
water content (%)	0–30	hydrogen (%)	2–7
TOC ^a (%)	40–90	nitrogen (%)	<0.5–1
viscosity ^b (cps)	34–6600 (40 °C)	oxygen (%)	1–33
density ^c (g/mL)	1.06–1.43 (24 °C)	sulfur (%)	0.4–4
MW ^d	230–780 ^e	cyanide (mg/kg)	<1–580 ^h
			<1–150 ⁱ
organic compds	range (mg/kg)	metals anal.	range (mg/kg)
monocyclic	13–25300	arsenic	3–23
polycyclic		beryllium	<1
2 and 3 rings	6800–218000	cadmium	<1–4
>3 rings	12000–110000	lead	1–930
NPAHs ^f	70–1000	nickel	2–74
SPAHS ^g	0–4000	selenium	<1–5
		vanadium	6–230
		chromium	<1–230

^a Total organic carbon. ^b Test methods ASTM D445 and D88. ^c Test methods ASTM D70, D369, or D1429. ^d Average molecular weight determined using vapor pressure osmometry. ^e Exception: asphaltene-like tar 1600. ^f Nitrogen polyaromatic hydrocarbons. ^g Sulfur polyaromatic hydrocarbons. ^h Determined using EPA method 4500. ⁱ Determined using EPA method 9010.

bration vessel and the cap were rinsed with methylene chloride into a 100-mL volumetric flask and brought to volume. Dissolved coal tar samples were filtered (0.45 μm) prior to analysis. For the coal tar samples from which it was difficult to remove residual water without loss (i.e., thin liquid coal tars), an aliquot of the neat coal tar was sampled for analysis as well.

Chromatographic Analysis. PAH concentrations in the coal tar and aqueous phases were determined using a gas chromatograph (GC) equipped with an ion trap detector (ITD). The GC/ITD method included a HP Ultra 2 column (95% methyl, 5% phenyl polysiloxane, 0.5-μm thickness; 30 m × 0.32 mm i.d.), helium as a carrier gas at a flow rate of approximately 1.0 mL/min, temperature gradient program, and an ion trap detector. The temperature gradient program consisted of a 1-min hold at 50 °C, a ramp to 130 °C at 30 °C/min followed by a 3-min hold, a ramp to 180 °C at 12 °C/min followed by a 1-min hold, a ramp to 240 °C at 7 °C/min, and a ramp to 300 °C at 12 °C/min followed by a 35-min hold. The ITD was set at an electron energy of 70 eV and scanned from 45 to 450 amu at 2 scans/s. The electron multiplier voltage was 1650 V, and the transfer temperature from the GC was 280 °C. Prior to GC analysis, samples were usually spiked with an internal standard consisting of naphthalene-*d*₈ and anthracene-*d*₁₀.

Results and Discussion

Coal Tar Composition. The coal tars used in this study were received from META Environmental, Inc. Various physical and chemical properties of these coal tars had been characterized (5), including density, viscosity, water and ash content, average molecular weight, and elemental and organic analysis. The ranges observed for these properties in terms of percentages or concentrations are summarized in Table II.

The viscosity of the coal tars ranged from approximately 34 to 6600 cps (40 °C), with the coal tar consistency varying from thin liquids (ID 1, 4, and 5) to thick liquids (ID 7) and from soft (ID 3 and 9) to sticky (ID 2) "taffy-like" materials. Coal tar viscosity will generally increase with

aging and decrease with temperature. Some coal tars had high ash contents, suggesting the presence of other solids. For example, coal tar ID 7N had a high content (37%) of what appeared to be sand and silt. The PAH concentrations for this coal tar were corrected to represent the mass of PAHs present per actual mass of coal tar. For the remaining coal tars an occasional rock or pellet was found, which was easily removed prior to experimentation.

Water content of the thin liquid coal tars was small (<1% mass basis). For the more viscous coal tars, reported water contents were as high as 30% (mass basis); however, high molecular weights and densities for these coal tars strongly suggest that these high water contents were in actuality a sampling artifact. It appears that water may have been trapped as a separate liquid phase within the taffy-like matrix of the coal tar.

Similar compounds were found in all of the tars, but individual hydrocarbon concentrations varied significantly from one MGP site to another. PAH concentrations ranged from 7000 to 220 000 mg/kg, with various naphthalenes as the dominant components. Several monocyclic aromatic hydrocarbons [e.g., benzene, toluene, ethylbenzene, and xylenes (BTEX) and styrene] were also present in concentrations ranging from 13 to 25 300 mg/kg. Much smaller amounts of nitrogen- and sulfur-containing aromatic hydrocarbons (e.g., carbazole and dibenzothiophene) were also found.

It is important to recognize that less than 40% (on a mass basis) of the coal tar constituents can be quantified (see Table II) using common extraction and chromatographic techniques. The unidentified tar fraction is often referred to as the "pitch" for operational purposes. Current sophisticated analytical techniques still lack the capability needed to identify most of the pitch constituents; however, their general nature may be surmised based on coal composition [e.g., Whitehurst et al. (6)] or oil composition. A majority of the pitch constituents are aromatic compounds with high molecular weights and low aqueous solubilities; thus, they may not be of direct concern in terms of groundwater contamination. However, the physical and chemical characteristics of the pitch may exert a strong influence on the rates of release and the equilibrium partitioning of the more-soluble tar constituents (e.g., BTEX, naphthalenes) that are of greater environmental concern. Also, nitrogen- and sulfur-containing aromatic hydrocarbons present in coal tars may impart nonideal behavior.

Tar-Water Partitioning. The success in applying a model based on Raoult's law for gasolines (4) and diesel fuels (3) led us to investigate whether ideal behavior could also be assumed for coal tars. Compared to gasolines and diesel fuels, coal tars are compositionally more complex; thus, greater deviations from ideal behavior might be expected. Gasolines, diesel fuels, and coal tars collected from different sites vary greatly in their composition, but only a small variation exists in the average molecular weights of the different gasolines (4) and diesel fuels (3). In contrast, different coal tars exhibit a wide range in average molecular weight and density (Table II).

The assumption of ideal behavior for coal tar is postulated here for practical expediency, since it reduces the number of parameters needed to estimate PAH concentrations in groundwater. Ideal behavior is not necessarily expected for such materials, but it is hoped that the assumption will be adequate within a specified acceptance factor; we have chosen here a factor of 2 to be adequate for field-scale applications. Experimental measurements of tar-water partition coefficients are difficult and are

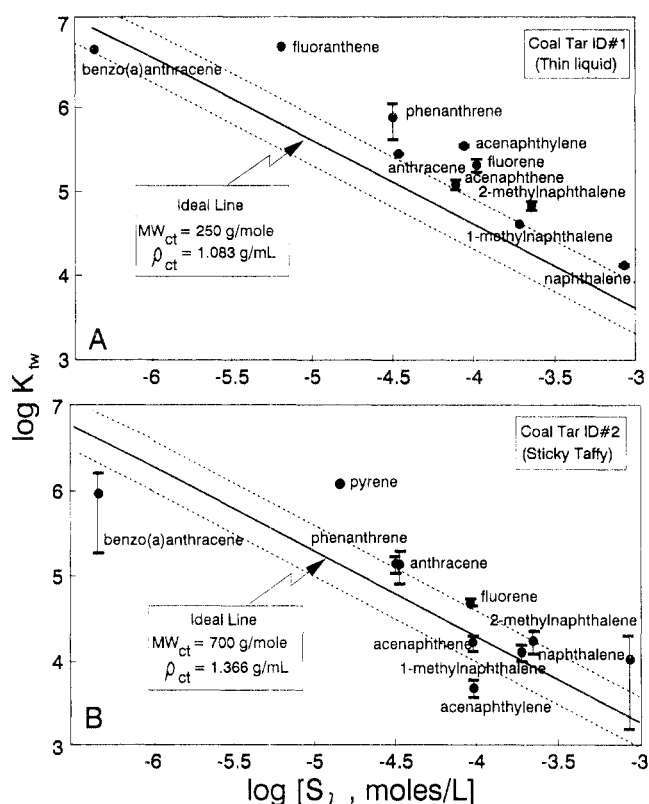


Figure 1. Comparison of measured tar-water partition coefficients (K_{tw}) and predictions based on Raoult's law for ID 1 (A) and ID 2 (B) coal tars.

subject to significant errors. Thus, experimental artifacts as a possible cause must be eliminated before nonideal behavior is attributed to a given coal tar or even to one or more constituents within a coal tar. It is with this pragmatic perspective that we will interpret tar-water partitioning data. The investigations of tar-water partitioning involved analysis of data collected in this study for eight tars, analysis of published data, and theoretical analysis of solute-solute interactions that might lead to nonideal behavior.

Analysis of Laboratory Data. In assessing the application of Raoult's law to compositionally complex mixtures, it is expedient to use the partition coefficients for the components between the organic and water phases. The use of partition coefficients facilitates examining the ideality of the entire system in a single, graphical representation. Application of Raoult's law and the assumption of ideal behavior yields the following relationship:

$$\log K_D = -\log S_1 - \log (MW_o/\rho_o) \quad (2)$$

where the ratio of the average molecular weight (MW_o , g/mol) and the density (ρ_o , g/L) of the organic phase is just the molar volume of the organic phase (\bar{V}_o). A derivation of eq 2 is provided by Lee et al. (3). It is evident from eq 2 that a linear inverse relationship exists between $\log K_D$ and $\log S_1$ where the slope is -1 and the intercept is dependent on the ρ_o and MW_o of the particular organic mixture. Using this relationship, the assumption of ideal behavior can be conveniently assessed for a complex mixture with a minimal number of easily obtained parameters.

The tar-water partitioning data for the eight tars examined in this study are presented in Figures 1-4. The logarithm of the average K_{tw} value and the calculated standard deviations are shown along with the prediction based on eq 2 (solid line) and the factor of 2 tolerance

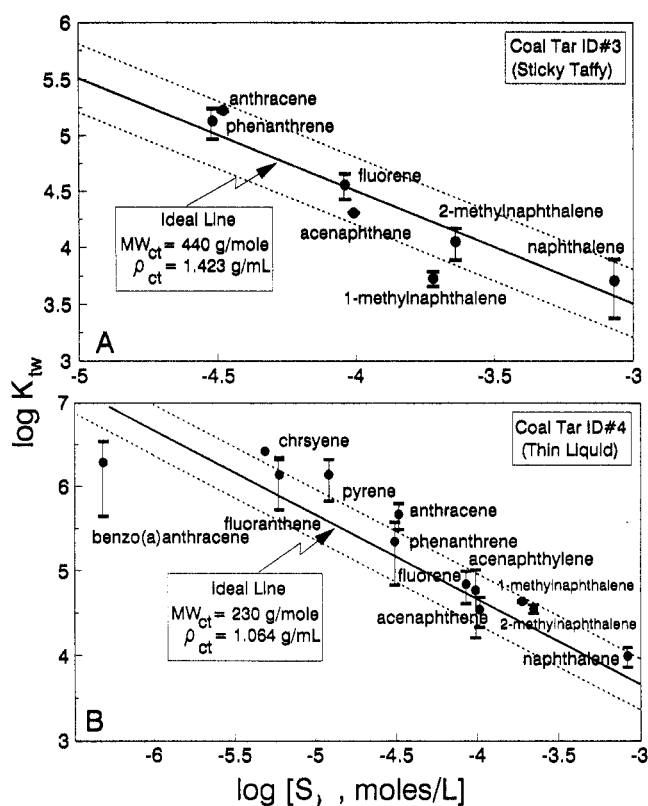


Figure 2. Comparison of measured tar-water partition coefficients (K_{tw}) and predictions based on Raoult's law, for ID 3 (A) and ID 4 (B) coal tars.

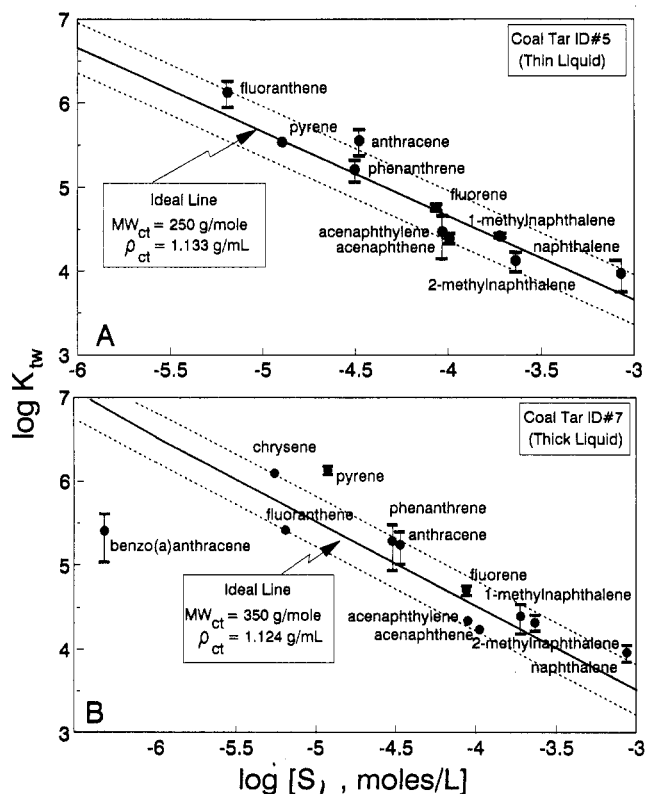


Figure 3. Comparison of measured tar-water partition coefficients (K_{tw}) and predictions based on Raoult's law, for ID 5 (A) and ID 7 (B) coal tars.

intervals. For most coal tars, the data points are scattered about the ideal line, suggesting that the assumption of ideal behavior suffices (again, within a factor of 2 error) in predicting K_{tw} for the PAHs. For the one exception (ID

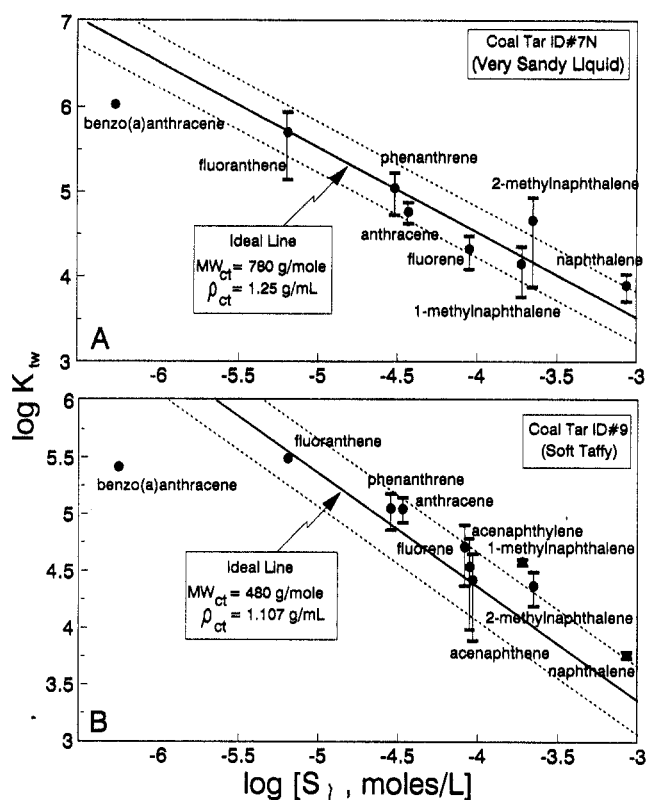


Figure 4. Comparison of measured tar-water partition coefficients (K_{tw}) and predictions based on Raoult's law, for ID 7N (A) and ID 9 (B) coal tars.

1), measured data points lie consistently above the ideal line (Figure 1A) indicative of an error in the estimate of the molar volume. Specific causes for the systematic deviation observed with coal tar ID 1 need to be further explored.

Benz[a]anthracene is the only PAH that consistently lies substantially below the ideal line for most of the coal tars. Uncertainties arising from both analysis and parameter estimation may have resulted in the observed negative deviations. Analysis of benz[a]anthracene in the aqueous phase approached detection limits, thus contributing to uncertainties. A greater source of error was probably incurred in the estimation of the supercooled liquid solubility for benz[a]anthracene. The S_l values (given in Table I) used in plotting $\log K_{tw}$ values in Figures 1-4 (given in Table I) were estimated by assuming a constant entropy of fusion (ΔS_f) (5). For most compounds, this method may be preferred over attempts to find reliable measured ΔH_f values needed for a direct calculation. However, in the case of benz[a]anthracene, the S_l values estimated using the average ΔS_f value was ≈ 1 order of magnitude higher than that calculated using the ΔH_f value reported by Choi et al. (11). Thus, the reasons for the observed deviation of benz[a]anthracene data points from the ideal line are indeterminate.

Analysis of Literature Data. The tar-water partition coefficients (K_{tw}) for several PAHs compiled from the literature (7-9) for three different coal tars are plotted in Figure 5 in a manner similar to Figures 1-4. For each coal tar, the ideal line (solid line) shown was calculated from eq 2 using the best estimates available for MW_{ct} and ρ_{ct} . For the coal tar investigated by Rostad et al. (7) (Figure 5A), the ideal line was calculated using the ρ_{ct} reported and a MW_{ct} value estimated from a weighted average of the mole fraction and molecular weight of each known component. For the unknown fraction, an average molecular weight of 300 was assumed. Picel et al. (9) reported values

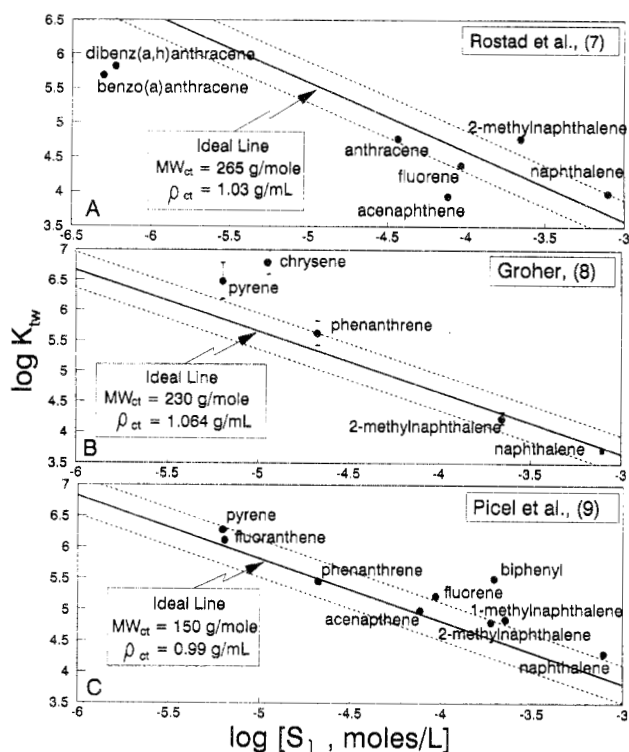


Figure 5. Comparison of measured tar-water partition coefficients (K_{tw}) reported in the literature and predictions based on Raoult's law. Literature source as indicated.

for both ρ_{ct} and MW_{ct} . Groher (8) did not report values for MW_{ct} and ρ_{ct} ; therefore, data for a coal tar, similar in composition, obtained from the same site a few years later were used to estimate the ideal line (Figure 5).

For most of the PAHs, the measured K_{tw} values are within a factor of 2 from the ideal line, with the best agreement observed for the Picel et al. (9) data (Figure 5C). Observed deviations from the ideal line could be the result of considerable nonideality in the tar-water system or a consequence of various experimental artifacts including inadequate time for equilibration and poor recovery of the PAH from the aqueous phase. The probability of such experimental artifacts increases for the larger PAHs where a greater difficulty is often encountered in accurately measuring the solubility of rather insoluble compounds.

A decrease in the measured K_{tw} values would be anticipated for deviations resulting from sufficient nonideality, as observed in Figure 5A for the Rostad et al. (7) data. The expectation of the presence of nonideality resulting in negative deviations for PAHs is based on work by Chiou and Schmedding (10) and Choi et al. (11), where the activity coefficients of several PAHs were measured in water-saturated octanol and mixtures of benzene and cyclohexane. In both cases, the activity coefficient of a given PAH in the organic phase (γ_o^*) was found to be greater than unity. For a mixture which is complex in composition and behaves in a "nonideal" fashion, the partition coefficient (K_D) between an organic liquid and an aqueous phase can be related to the aqueous solubility of the pure liquid (S_1) in the following manner (10):

$$\log K_D = -\log S_1 - \log \bar{V}_o - \log \gamma_o^* \quad (3)$$

assuming the presence of other components in the aqueous phase is ignored (12). Note that any deviations due to nonideal behavior will arise from the last term on the right-hand side of eq 3. Therefore, γ_o^* values greater than unity will result in values of $\log K_D$ smaller than those estimated by assuming ideal behavior.

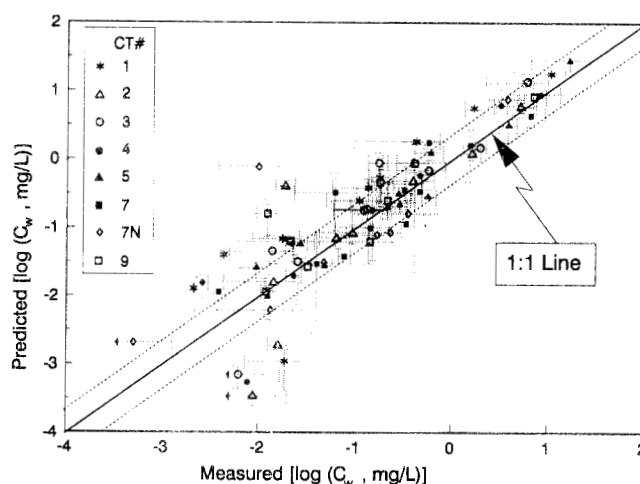


Figure 6. Comparison of laboratory-measured aqueous-phase concentrations (C_w) with those predicted on the basis of Raoult's law for eight coal tars.

Predicting Aqueous-Phase PAH Concentrations.

The $\log K_{tw}$ vs $\log S_1$ relationship observed for several coal tars (Figures 1-4) suggests that the application of Raoult's law and the assumption of ideal behavior may be adequate to predict the concentration of PAHs in groundwater (C_w) in contact with a coal tar source. Equation 1 was used to estimate the concentrations of several PAHs expected to be present in a groundwater in equilibrium with a coal tar. The mole fraction of the PAH in the organic phase (x_o) needed in eq 1 was approximated by the product of the mass fraction (mg/g) in the coal tar and MW_{ct} (i.e., $C_w = M_i MW_{ct} S_1$). A log-log plot comparing predicted aqueous concentrations (converted to commonly reported units of mg/L) and those measured during the laboratory partitioning studies is shown in Figure 6. The error bars shown in Figure 6 for the laboratory-measured concentrations represent the standard errors calculated from replicate averages. An arrowhead on an error bar indicates that the lower bound approached the limit of detection. For the predicted concentrations, the error bars shown in Figure 6 were estimated from the standard errors calculated from the replicate average of M_i . Also given in Figure 6 is the 1:1 line with the corresponding factor of 2 tolerance intervals.

Confidence in the C_w values predicted using eq 1 is dependent on several factors other than the premise of ideal behavior, including uncertainty about the input parameters (e.g., M_i , MW_{ct} , and S_1). Both M_i and MW_{ct} can be determined experimentally; therefore, errors associated with these parameters can be obtained from replicate analysis information. Sampling and chromatographic analysis of this heterogeneous liquid waste is prone to considerable errors; therefore, the deviation associated with M_i is probably the greatest source of error in estimating C_w values.

A majority of the data presented in Figure 6 lie within the factor of 2 intervals given about the 1:1 line. The data that lie outside the factor of 2 intervals result in predicted concentrations greater than those measured, with the exception of the data points below the 1:1 line which correspond to benz[a]anthracene. Benz[a]anthracene is present in small amounts in coal tar, often approaching the limits of analytical detection. In addition, aqueous solubility measurements for compounds with small values (i.e., $<10^{-2}$ mg/L) become increasingly less reliable. Good agreement for a majority of PAHs within a factor of 2 suggests that the use of eq 1, based on Raoult's law, may be adequate for estimating PAH concentrations. At the

Table III. Maximum C_w Values for Several PAHs Based on the Data Compiled for Eight Coal Tars

compound	S_w (mg/L)	maximum C_w^a	C_w/S_w
naphthalene	32	14 ^b	0.44
1-methylnaphthalene	27	2	0.05
2-methylnaphthalene	26	1.4	0.05
acenaphthylene	3.93	0.5	0.13
acenaphthene	3.42	0.3	0.1
fluorene	1.9	0.3	0.16
phenanthrene	1.0	0.4	0.3
anthracene	0.07	S_w	1.0
fluoranthene	0.27	0.01	0.4
pyrene	0.16	0.1	0.5
benz[a]anthracene	0.0057	S_w	1.0
chrysene	0.006	S_w	1.0
benzo[a]pyrene	0.0038	0.001	0.3

^a $T = 25^\circ\text{C}$. ^b Result from data compiled for seven of the eight coal tars; data for one tar resulted in a prediction of 26 mg/L.

very least, aqueous concentrations estimated using this approach should be considered more appropriate and definitive than merely assuming crystal solubilities for aqueous-phase concentrations.

Given the variations that may exist in (1) the different coal tar deposits at a given site and (2) the extent of weathering at that site, it would be advantageous to estimate maximum PAH concentrations that might be found at any site. In order to estimate maximum C_w values, the eight coal tars investigated were assumed to be representative of coal tars that might be found at any site in the United States. The maximum concentrations of the PAHs investigated, based on the data compiled for the eight coal tars, are given in Table III along with the ratios of C_w to S_w . Note that the maximum C_w expected is the crystal aqueous solubility for anthracene, chrysene, and benz[a]anthracene.

In the absence of cosolvents and other solubility-enhancing adjuvants (e.g., dissolved organic carbon, surfactants, etc.), the maximum aqueous-phase concentration (C_w) is limited by the crystal solubility (S_w). Although the hypothetical supercooled liquid solubility is used to obtain best estimates for C_w , mixing of the chemical with the aqueous phase is ultimately governed by interactions with the solvent. These are expressed through the crystal solubility (S_w) (13). For a PAH that has a low aqueous solubility and a high melting point and is present in high concentration in the coal tar, the concentration predicted in the aqueous phase by assuming ideal behavior would be the crystal aqueous solubility (S_w).

Summary

Release of polycyclic aromatic hydrocarbons from coal tar disposed at former MGP sites is governed primarily by solubility. A common assumption made by utility industry and regulatory agency personnel in assessing the likelihood of soil and water contamination from coal tar has been that PAH concentrations in groundwater would be equal to the corresponding aqueous solubilities of the pure compounds. This assumption may not be valid for complex organic wastes (e.g., gasoline, diesel fuel, and coal tar) which are mixtures of a large number of hydrocarbons and usually leads to considerable overpredictions of the PAH concentrations likely to be found in groundwater.

According to the model based on Raoult's law, the concentration of an organic constituent in the aqueous phase in equilibrium with an "ideal" organic mixture is proportional to the mole fraction of that constituent in the organic phase. Our analysis of published and new data for

liquid-liquid partitioning of hydrocarbons from gasolines, diesel fuels, and several coal tars suggests that deviations from ideal behavior are within a factor of 2 or less in most cases.

Agreement between the model predictions based on Raoult's law and measured liquid-liquid partitioning data for several PAHs is not to be taken as evidence that coal tars are indeed ideal mixtures. Rather, the assumption of ideal behavior might suffice for practical considerations in providing first-order estimates for maximum PAH concentrations likely to be found in groundwater leaving a coal tar source.

Acknowledgments

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Registry No. Naphthalene, 91-20-3; 1-methylnaphthalene, 90-12-0; 2-methylnaphthalene, 91-57-6; acenaphthylene, 208-96-8; acenaphthene, 83-32-9; fluorene, 86-73-7; phenanthrene, 85-01-8; anthracene, 120-12-7; fluoranthene, 206-44-0; pyrene, 129-00-0; chrysene, 218-01-9; benz[a]anthracene, 56-55-3; benzo[a]pyrene, 50-32-8.

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