

## Risk Assessment for Polycyclic Aromatic Hydrocarbon NAPLs Using Component Fractions

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Polycyclic aromatic hydrocarbons (PAHs) are important environmental contaminants because of their suspected carcinogenicity. PAH contamination is often found in the form of nonaqueous phase liquids (NAPLs), such as coal tar. These materials are very complex mixtures with the constituent compounds exhibiting a wide range of chemical, physical, and toxicological properties. This makes it difficult to characterize a PAH NAPL and predict its behavior. Lumped metrics, such as total petroleum hydrocarbons (TPH), are often used to specify remediation goals at PAH NAPL sites, but these metrics do not capture the variation in NAPL composition over time and as such do not consider changes in risk over time. This paper presents an alternative method for characterizing PAH NAPLs that is based on the fraction approach developed by the Total Petroleum Hydrocarbon Criteria Working Group (TPHCWG). The fraction approach characterizes the PAH NAPL as a collection of U.S. EPA Priority Pollutants plus hydrocarbon fractions. This approach allows prediction of the NAPL compositional dynamics while retaining some of the simplified analysis of a lumped parameter approach. The fractions and priority pollutants are modeled as NAPL components for performing risks assessments and assessing the potential of remediation strategies. This makes the fraction approach amenable for use in a Risk-Based Corrective Action (RBCA) framework. In this work, the TPHCWG fraction approach was modified for description of NAPL constituents that are solids in their pure states. This was accomplished by assigning an equivalent solid-liquid reference fugacity ratio for each fraction. Thirty-year simulations with two model coal tars are presented, comparing the risk calculations for the fraction approach to those accounting for the complete NAPL composition. These simulations show that the model using the fraction approach predicts similar NAPL compositional dynamics and PAH carcinogenic risk as the model describing all the compounds. Use of the fraction approach at PAH NAPL sites will allow a more accurate accounting of the risk variation than the TPH approach. Additionally, it will emphasize development and use of remediation methods that address risk reduction, not just the reduction in total contaminant mass.

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### Introduction and Background

Polycyclic aromatic hydrocarbons are an important class of environmental pollutants. Their presence in the environment is of concern because the U.S. Environmental Protection Agency (U.S. EPA) and the National Institute of Environmental Health Sciences (NIEHS) have classified a number of PAHs as probable human carcinogens (1, 2). PAHs are present at numerous sites with environmental contamination; one major group of which is manufactured gas plant (MGP) sites that produced a combustible gas from coal, coke, and/or oil. A major byproduct of the coal gasification process was coal tar, a dense, viscous nonaqueous phase liquid (NAPL) that contains up to 75% PAHs by mass (3). The coal tar produced at manufactured gas plants was usually sold, recycled, or used as fuel within the plant or placed on- or off-site in holding tanks, trenches, or ponds where it would not interfere with day-to-day operations (4, 5). Given these practices, there may be areas of PAH NAPL contamination existing below ground at most MGP sites (6).

In 1985, the U.S. EPA reported that there is evidence of approximately 1500 MGP sites in the United States. Hatheway (6) extended the scope of the EPA report to include plants in operation for less than a decade; those used for private industry; and those used for large complexes such as prisons, hotels, colleges, and military posts. Hatheway suggests that, when considering the entire range of locations at which coal was partially combusted, the number of sites is greater than 32 000. Whether the actual number is closer to U.S. EPA's estimate or to Hatheway's estimate, either presents a large number of sites with potential PAH NAPL contamination that may require remediation.

Environmental remediation of PAH NAPLs, such as coal tar, poses scientific, technological, and regulatory challenges due to their wide range of physical, chemical, and toxicological properties. The physical and chemical properties of PAHs, such as solubility, volatility, and biodegradability, have the general trend of recalcitrance increasing with molecular weight (MW). For example, the aqueous solubilities of the U.S. EPA Priority Pollutant PAHs range from 31 mg/L for naphthalene (MW = 128) to  $3 \times 10^{-4}$  mg/L for benzo[*g,h,i*]perylene (MW = 276) (7). An important consideration with PAH NAPLs is that the aqueous concentration of an individual PAH is a direct function of its relative abundance in the NAPL phase. A detailed discussion of this is presented in Peters et al. (7). However, the main point can be summarized in the following equation:

$$C_i^* = \frac{x_i^N}{(f^S/f^L)_i} C_{S,i} \quad (1)$$

Here,  $C_i^*$  is the aqueous-phase solubility of compound  $i$ ,  $x_i^N$  is the mole fraction of compound  $i$  in the NAPL,  $C_{S,i}$  is the aqueous solubility of the pure compound  $i$ , and  $(f^S/f^L)_i$  is the solid-liquid reference fugacity ratio for the compound. The main implication of eq 1 is that change in the NAPL composition over time, whether due to weathering or active remediation, can cause dramatic changes in the aqueous concentration of PAHs.

In Peters et al. (7), we showed that it is necessary to account for PAH NAPL compositional changes over time in order to estimate carcinogenic health risk and to evaluate the effectiveness of remediation technologies in reducing this risk. Unfortunately, PAH NAPLs can consist of hundreds of

separate compounds, and this large number makes it extremely difficult and expensive to comprehensively determine the composition of a sample taken in the field. For example, Peters and Luthy (3) presented a gas chromatograph/mass spectrometry (GC/MS) analysis of coal tar taken from a MGP site in Stroudsburg, PA. That analysis, while fairly comprehensive, was able to determine only 40 specific compounds and 4 groups of compounds, accounting for approximately 46% of the total NAPL by weight. This type of detailed GC/MS analysis is too time-consuming and costly for routine environmental sample analysis. A simpler analysis can be done to quantify only the 17 Priority Pollutant PAHs, but these compounds may account for a relatively small portion of the total NAPL.

Because of these difficulties in characterizing PAH NAPLs, remediation goals are often specified in terms of lumped parameters, such as total petroleum hydrocarbons (TPH) or total PAHs (TPAH) (8, 9). While these lumped parameters greatly simplify the analysis required at contaminated sites, risk assessments based on these metrics assume a fixed NAPL composition. With this assumption, the selection of a remediation strategy defaults from one of reducing risk to one of reducing mass. This leads toward selection of remediation strategies that preferentially remove the readily soluble, biodegradable, and/or volatile lower molecular weight PAHs, while leaving the higher molecular weight PAHs in the subsurface. Depending on site-specific conditions, this can result in remediation goals that under- or overestimate the true long-term risks associated with the NAPL.

For example, remediation technologies specified in the U.S. EPA Records of Decision (RODs) for the 12 MGP sites on the National Priorities List include ex situ remediation via removal of soil for incineration, disposal, washing, or bioremediation and in situ remediation via pump-and-treat and bioremediation. The only other in situ remediation technology that is specified is hot water injection at the Broadhead Creek MGP site in Stroudsburg, PA. None of the conventional in situ techniques required by these RODs are effective in removing the higher molecular weight PAHs in the coal tars. It may be the case that the remaining higher molecular weight PAHs do not pose any appreciable risk because of their limited mobility. However, the NAPL compositional changes must be considered in order to determine if this is true. Neglecting temporal changes in NAPL composition may result in remediation activities that continue for many years with no appreciable reduction of the long-term risks.

The purpose of this paper is to present an alternative method to TPH for characterizing PAH NAPLs, which requires reasonable analytical and numerical analysis while maintaining an accounting of the NAPL composition for PAH compounds of interest (e.g., the 17 U.S. EPA Priority Pollutants PAHs). The method presented is an extension of the fraction approach developed by the TPHCWG for performing risk assessments of hydrocarbon mixtures (9). The TPHCWG fraction approach was designed to be implemented in a risk-based corrective action (RBCA) framework, such as the ASTM standard guide for RBCA applied at petroleum release sites (10). The paper begins with a description of a modified TPHCWG fraction approach for PAH NAPLs and follows with a demonstration of the applicability of this approach to risk assessments through numerical simulations of composition dynamics for two complex PAH NAPLs. These simulations use the modeling approach for multicomponent PAH NAPLs presented by Peters et al. (7).

## Development of a Fraction Approach That Accounts for PAH NAPL Complexities

**TPHCWG Fraction Approach.** In the early 1990s, state governments and professional organizations began to rec-

**TABLE 1. TPHCWG Hydrocarbon Fractions Derived from Fate and Transport Characteristics and Their Associated Properties<sup>a</sup>**

EC range	solubility (mg/L)	vapor pressure (atm)	log ( $K_{oc}$ ) <sup>b</sup> (mg/L)	solid-liquid ref fugacity ratio <sup>c</sup>
<b>Aliphatic</b>				
C5-C6	36.0	0.35	2.9	1
>C6-C8	5.4	0.063	3.6	1
>C8-C10	0.43	0.0063	4.5	1
>C10-C12	0.034	0.00063	5.4	1
>C12-C16	0.00076	0.000048	6.7	1
>C16-C21	0.0000025	0.0000011	8.8	1
<b>Aromatic</b>				
C5-C7	1800	0.13	1.9	1
>C7-C8	520	0.038	2.4	1
>C8-C10	65	0.0063	3.2	0.942
>C10-C12	25	0.00063	3.4	0.649
>C12-C16	5.8	0.000048	3.7	0.371
>C16-C21	0.65	0.0000011	4.2	0.160
>C21-C35	0.0066	0.0000000044	5.1	0.027
>C21-C28	0.036	0.0000000079	4.8	0.052
>C28-C35	0.0012	$2.4 \times 10^{-11}$	5.5	0.014

<sup>a</sup> Italicized values show modifications to TPHCWG fractions that facilitate modeling of PAH NAPLs. From ref 12, except as noted.

<sup>b</sup> Partition coefficient of the hydrocarbon fraction between water and soil, normalized by the organic carbon content of the soil. <sup>c</sup> Calculated from regression shown in Figure 1.

ognize the fact that existing regulatory frameworks did not address the complexities of hydrocarbon contamination in the subsurface. This awareness came from the recognition that using a TPH approach at hydrocarbon sites did not give a realistic picture of the health risks, as the composition of the hydrocarbon was not considered in the analysis, and that existing State and Federal regulations for remediating hydrocarbon contaminated sites had little scientific or health risk basis (8, 9, 11).

To address these concerns, the Massachusetts Department of Environmental Protection (MADEP) developed an approach that estimates health risks based on the composition of a hydrocarbon source, while realizing that it was effectively impossible to require analysis for all compounds within the mixture (8, 11). Their approach entails dividing the hydrocarbon contamination into measurable fractions, with the number of fractions determined solely by toxicity considerations. The benefit of the fraction approach over the TPH approach is that it provides much more information regarding the composition and toxicity of a hydrocarbon source, while retaining the analytical simplicity of lumped approaches. Recently, the TPHCWG has extended the MADEP fraction approach by redefining the fractions based on fate and transport considerations (9, 12, 13).

The TPHCWG fraction approach divides a hydrocarbon source into aliphatic and aromatic fractions. These two groups are then further divided based on their equivalent carbon number (EC), which is related to the boiling point of a chemical normalized to the boiling point of the *n*-alkanes or can be determined via the retention time of the compounds in a boiling point gas chromatography (GC) column (12, 14). This is how analytical laboratories typically report carbon numbers for chemicals determined with a boiling point GC column and is consistent with methods utilized in the petroleum industry for separating complex mixtures (12). Parameters, such as noncarcinogenic toxicity, volatility, and solubility were then defined for each fraction using correlations with the equivalent carbon number (12, 13). This allows the fractions to be used in fate and transport models, with each fraction treated as a single compound. The fractions and their associated fate and transport parameters developed by the TPHCWG are presented in Table 1. For PAH NAPLs,

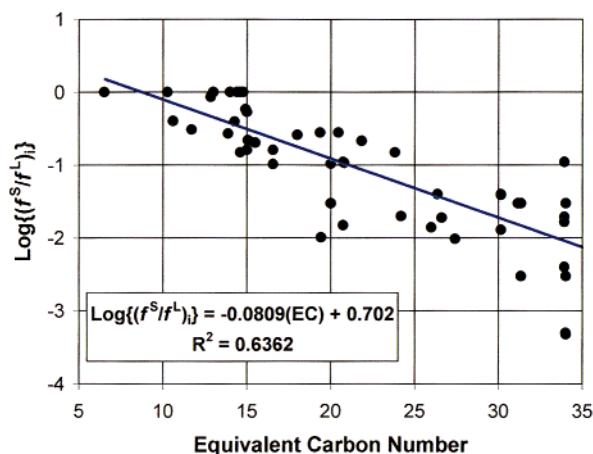


FIGURE 1. Log-linear regression fit to the solid-liquid reference fugacity ratio as a function of equivalent carbon (EC) number was used to determine the reference fugacity ratios for the fractions. Data were taken from the PAHs included in Table 2.

such as coal tars, only the aromatic fractions are necessary. It is important to note that the TPHCWG assumes that the uncharacterized fractions (i.e., equivalent carbon numbers >21 for the aliphatics and >35 for the aromatics) are insoluble. The uncharacterized fractions are representative of the high molecular weight material that cannot be characterized using standard chromatographic methods. Despite the fact that these fractions may contain hazardous compounds, the assignment of zero solubility implies they will not contribute to the risk from consumption of contaminated water. The uncertainty associated with the uncharacterized fractions is a limitation of any compositional approach.

The approach used by the TPHCWG to consider health risks when fractionating a hydrocarbon source is to examine carcinogenic and noncarcinogenic risks independently (13). Noncarcinogenic effects are defined for each fraction, based on the assumption that like molecules have similar health effects. Carcinogenic effects are evaluated through the identification and quantification of separate indicator compounds, such as benzene and those PAHs that are classified as carcinogenic (e.g., PAHs on the U.S. EPA Group B2 carcinogen list). The approach used by the U.S. EPA to quantify PAH carcinogenicity is to relate carcinogenicity to that of benzo[a]pyrene through the use of toxic equivalency factors (TEFs) (2) [a summary of this approach is given by Peters et al. (7)]. In the TPHCWG approach, any remaining EPA priority PAH pollutants that have not been assigned TEFs are also characterized separately and included as indicator compounds (their TEFs are assumed zero in the carcinogenic risk calculations). These indicator compounds are not included in the hydrocarbon fractions. Thus, the number of compounds that must be quantified is the sum of the number of fractions and the number of indicator compounds.

**Application to PAH NAPLs.** The TPHCWG fraction approach was not developed specifically for use with NAPLs. We present two modifications to make the fraction approach applicable for PAH NAPLs. The first modification derives from eq 1, where the aqueous solubility of a compound that is solid in its pure state is a function of its solid-liquid reference fugacity ratio. A reference fugacity ratio was assigned for each fraction, using the same method used by the TPHCWG for determining the other fraction parameters (12). PAH reference fugacity ratios were plotted as a function of EC, and a log-linear regression was applied to the data (Figure 1). Then, the median EC for each fraction was used

with the regression to estimate an equivalent reference fugacity ratio (Table 1).

The second modification splits the >C21-C35 aromatic fraction into two fractions. When considering PAH NAPLs, the several order of magnitude span of the aqueous solubilities and fugacity ratios in the >C21-C35 range results in increased errors when modeling the higher molecular weight compounds. Thus, this aromatic fraction has been divided into >C21-C28 and >C28-C35 aromatic fractions. The appropriate parameters for each fraction were recalculated, based on the fraction's EC, using the TPHCWG equations for solubility, vapor pressure, and partition coefficient and the reference fugacity ratio equation given in Figure 1 (see Table 1). In addition, if noncarcinogenic risks are being considered, then the oral reference dose (RfD) for the two new aromatic fractions should be set equal to the TPHCWG oral RfD for the >C21-C35 aromatic fraction.

One aspect of PAH NAPL composition dynamics that is not well described with the fraction approach is the solidification of compounds as they reach their solubility limits within the NAPL phase. The mole fraction value of this solubility limit is well approximated by the solid-liquid reference fugacity ratio (7). In the fraction approach, the mole fraction is the sum of the mole fractions of a group of compounds, so it is not possible to predict the solidification of individual compounds within each grouping. Conceivably, one could predict the solidification of the entire fraction by comparing the fraction's mole fraction with a value representative of the fraction's NAPL phase solubility limit, but this value is difficult to predict without knowledge of the number of compounds in the group. This inability to accurately describe solidification of the components within the fractions is a limitation of the fraction approach that is of variable importance. The solidification process is of minor significance for unweathered NAPLs and for time periods of a few decades (e.g., simulations presented in ref 7). However, it may become important for extensively weathered NAPLs or for much longer time periods when the NAPL is depleted of a significant portion of the lower molecular weight compounds (15, 16).

## Analysis of the Fraction Approach through Numerical Simulations

**Numerical Simulations.** The applicability of the fraction approach to PAH NAPLs is demonstrated here through simulations of coal tar dissolution in an aquifer. The model used to perform the simulations is presented in detail by Peters et al. (7). Two different NAPL compositions were considered. The first (NAPL 1) is based on the low-saturation scenario examined by Peters et al. (7). For this NAPL, the composition is weighted toward the lower molecular weight PAHs and is representative of relatively unweathered coal tars (46% of the NAPL has a molecular weight <160). The second (NAPL 2) is weighted toward the higher molecular weight PAHs and can be considered representative of a weathered coal tar (only 20% of the NAPL has a molecular weight <160). Correspondingly, the uncharacterized fraction of the first NAPL is much smaller than that for the second. The compositions of the two model coal tars along with chemical property data are shown in Table 2.

The dissolution of the two NAPLs were simulated over a 30-year time span using the hydrologic and NAPL parameters presented in Peters et al. (7). First, the NAPLs were simulated using their complete compositions as shown in Table 2 (i.e., each of the PAHs is modeled, along with the uncharacterized fraction, which is modeled as an insoluble compound). Then the NAPLs were fractionated into the indicator compounds (Priority Pollutant PAHs and benzene) and the aromatic fractions, and the simulations were repeated. The purpose



TABLE 2. Example NAPL Compositions and Associated Parameters<sup>a</sup>

PAH	symbol	solid-liquid ref fugacity ratio <sup>b,c</sup>	aq solubility <sup>b,c</sup> (mg/L)	MW	effective C no. <sup>d</sup>	mole fraction in NAPL 1	mole fraction in NAPL 2
benzene	BEN	1	1780	78	6.5	0.03	0.001
indan	IND	1	100	118	10.27	0.001	0.001
naphthalene	NPH	0.31	31	128	11.69	0.17	0.004
1-methylnaphthalene	1MN	1	28	142	12.99	0.06	0.06
2-methylnaphthalene	2MN	0.86	24.6	142	12.84	0.08	0.06
acenaphthylene	ACY	0.22	3.9	152	15.06	0.04	0.01
acenaphthene	ACE	0.20	3.8	154	15.5	0.03	0.02
biphenyl	BP	0.39	7	154	14.26	0.007	0.007
1,3-dimethylnaphthalene	13DMN	1	8	156	14.77	0.001	0.001
1,4-dimethylnaphthalene	14DMN	1	11.4	156	14.6	0.001	0.001
1,5-dimethylnaphthalene	15DMN	0.27	3	156	13.87	0.001	0.001
2,3-dimethylnaphthalene	23DMN	0.16	2.5	156	15	0.001	0.001
2,6-dimethylnaphthalene	26DMN	0.15	1.65	156	14.6	0.001	0.001
1-ethylnaphthalene	1EN	1	10.7	156	14.41	0.006	0.006
2-ethylnaphthalene	2EN	1	8	156	13.99	0.03	0.03
fluorene	FLR	0.16	1.9	166	16.55	0.05	0.02
phenalene	PHNE	0.28 <sup>e</sup>	2.151	166	15.98	0.005	0.005
4-methylbiphenyl	4MBP	0.58	4.05	168	14.92	0.002	0.002
1,3,5-trimethylnaphthalene	135TMN	0.4	2	170	10.6	0.05	0.05
anthracene	ANTH	0.01	0.05	178	19.43	0.0085	0.007
phenanthrene	PHN	0.28	1.1	178	19.36	0.05	0.03
1-methylfluorene	1MFL	0.26	1.1	180	17.99	0.02	0.02
trans-1,2-diphenyl	tDPE	0.11	0.29	180	20	0.001	0.001
4,4'-dimethylbiphenyl	44DMP	0.10	0.175	182	16.55	0.001	0.001
bibenzyl	BBZ	0.54	4.4	182	15	0.001	0.001
diphenylmethane	DPM	1	15.25	188	14	0.001	0.001
1-methylphenanthrene	1MP	0.11	0.27	192	20.73	0.004	0.004
2-methylanthracene	2MA	0.015	0.04	192	20.73	0.004	0.004
9-methylanthracene	9MA	0.28	0.27	192	20.45	0.001	0.001
fluoranthene	FLN	0.21	0.26	202	21.85	0.02	0.003
pyrene	PYR	0.11	0.13	202	20.8	0.03	0.005
aceanthrylene	AAN	0.081 <sup>e</sup>	0.1502	202	22.17	0.003	0.003
9,10-dimethylanthracene	9,10DMA	0.03	0.06	206	20	0.001	0.001
benzo[a]fluorene	BaFL	0.02	0.045	216	24.2	0.001	0.001
benzo[b]fluorene	BbFL	0.15	0.002	216	23.83	0.001	0.001
methylpyrene	MPY	0.052 <sup>e</sup>	0.0533	216	24.57	0.04	0.04
benz[a]anthracene	BaA	0.04	0.011	228	26.37	0.005	0.003
chrysene	CHR	0.01	0.002	228	27.41	0.007	0.001
naphthacene	NPA	0.0005	0.001	228	34	0.00005	0.00005
triphenylene	TPN	0.019	0.04	228	26.61	0.001	0.001
acepyrene	APY	0.035 <sup>e</sup>	0.022	228	26.63	0.004	0.004
p-terphenyl	pTP	0.014	0.018	230	26	0.001	0.001
methylchrysene	MCH	0.023 <sup>e</sup>	0.0078	242	29.04	0.04	0.04
benzo[b]fluoranthene	BbFN	0.039	0.0015	252	30.14	0.003	0.001
benzo[j]fluoranthene	BjFN	0.04	0.003	252	30.14	0.001	0.001
benzo[k]fluoranthene	BkFN	0.013	0.0008	252	30.14	0.003	0.001
benzo[a]pyrene	BaP	0.03	0.004	252	31.34	0.006	0.008
benzo[e]pyrene	BeP	0.03	0.004	252	31.17	0.008	0.008
perylene	PERY	0.003	0.0005	252	31.34	0.0005	0.0005
7,12-dimethylbenzoanthracene	7,12DBA	0.11	0.05	256	33.92	0.0001	0.0001
9,10-dimethylbenzoanthracene	9,10DBA	0.11	0.0435	256	33.92	0.0001	0.0001
3-methylcholanthrene	3MCA	0.03	0.002	268	34.01	0.0001	0.0001
benzo[g,h,i]perylene	BghiP	0.003	0.0003	276	34.01	0.001	0.001
indeno[1,2,3-cd]pyrene	IPY	0.045	0.062	276	35.01	0.004	0.001
dibenz[a,c]anthracene	DBaCA	0.017	0.0016	278	33.92	0.0001	0.0001
dibenz[a,h]anthracene	DBaHA	0.004	0.0005	278	33.92	0.0006	0.0001
dibenz[a,j]anthracene	DBaJA	0.020	0.0012	278	33.92	0.0001	0.0001
benzo[a]chrysene (picene)	PIC	0.0071 <sup>e</sup>	0.0005	278	35.23	0.001	0.001
coronene	COR	0.0005	0.00014	300	34.01	0.00005	0.00005
uncharacterized	UCF	1		300		0.1598	0.5218
total characterized						0.8402	0.4782

<sup>a</sup> NAPL 1 is representative of a relatively unweathered coal tar and NAPL 2 is representative of a relatively weathered coal tar. Italicized compounds are on the U.S. EPA Priority Pollutant List. <sup>b</sup> All data at 25 °C. <sup>c</sup> Source: refs 7 and 22 unless otherwise specified. <sup>d</sup> As defined by the TPHCWG (12). <sup>e</sup> Obtained from regression shown in Figure 1.

of this comparison was to determine if the fraction approach is able to simulate both the NAPL compositional dynamics and the aqueous solubilities of the PAH indicator compounds that are predicted through use of the fully characterized NAPL.

Next, carcinogenic risks were calculated from the simulated aqueous concentrations to represent risk due to

consumption of drinking water directly contaminated with the PAH NAPLs. This paper focuses on carcinogenic risk, which has traditionally been the risk assessment basis for benzene and PAHs. A detailed discussion of noncarcinogenic health effects is provided in Volume 4 of the TPHCWG documentation (13). Lifetime carcinogenic risks were esti-

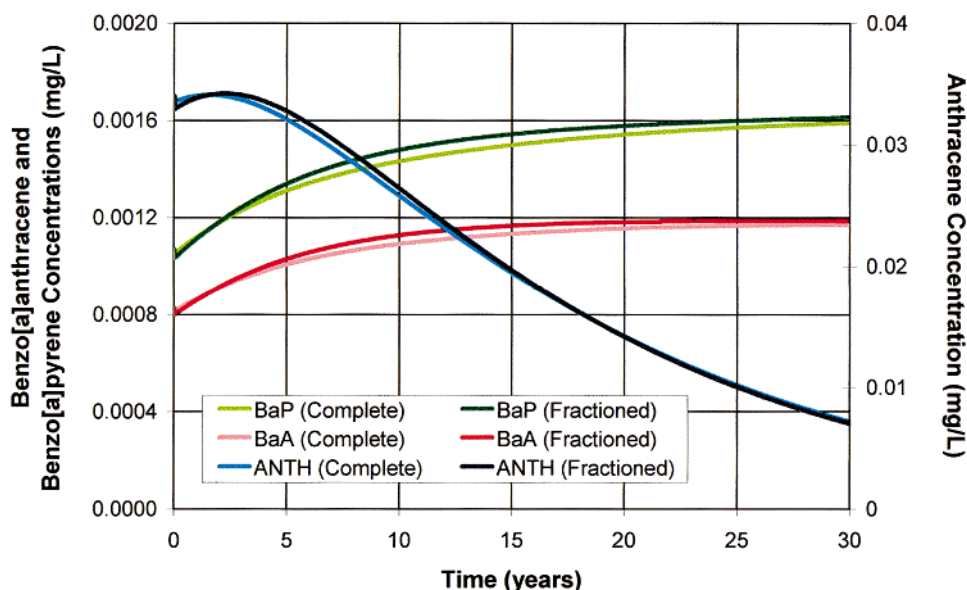


FIGURE 2. These simulations show that the model using the fraction approach provides similar PAH NAPL dynamics to the model utilizing all the compounds. Here, the aqueous concentrations of anthracene, benz[a]anthracene, and benzo[a]pyrene are shown as functions of time for the weathered NAPL (NAPL 2). It is seen that as the lower molecular weight PAHs are removed from the NAPL, the aqueous concentrations of the higher molecular weight PAHs increase due to their increasing mole fraction in the NAPL.

estimated for PAHs with TEFs using the method outlined in Peters et al. (7). The risk results from the fraction approach were compared to those predicted through simulation of the fully characterized NAPL. Also, a comparison was made for each simulation between the carcinogenic risks determined using the TEFs for the U.S. EPA Group B2 carcinogens (2) and using the TEFs for all the U.S. EPA Priority Pollutant PAHs presented by Nisbet and LaGoy (17). A discussion of the U.S. EPA Group B2 TEFs and the Nisbet and LaGoy TEFs is provided in Peters et al. (7).

**Simulation Results.** The aqueous concentrations for three representative PAHs, anthracene, benz[a]anthracene, and benzo[a]pyrene, are shown as a function of time in Figure 2 for NAPL 2. It is seen that the fraction approach provides excellent agreement with the results obtained from the complete simulation. Similar comparisons were found for NAPL 1 (data not shown). Additionally, Figure 2 demonstrates how the lower molecular weight compounds are removed from the system first. Then, as the mole fractions of the higher molecular weight compounds increase, their aqueous concentrations increase. The aqueous concentration of anthracene decreased over 75% at the end of 30 years, while the aqueous concentration of benzo[a]pyrene increased by more than 50%. This stresses the point that the NAPL compositional changes over time must be accounted for in order to estimate the PAH aqueous concentrations and, thus, the risk due to consumption of contaminated water for PAH NAPLs.

The contributions to carcinogenic risk by each of the indicator compounds for the two NAPLs along with the total carcinogenic risks are shown in Figure 3. The risk values plotted in the figure were computed using the TEF values of Nisbet and Lagoy, while the inset table shows the total risk values computed using both the U.S. EPA and the Nisbet and Lagoy TEF values. These results show that the model using the fraction approach provides similar PAH carcinogenic risk to the model utilizing all the compounds.

The results presented in Figure 3 show that there is not necessarily a direct correlation between toxicity and contribution to risk. The lower molecular weight PAHs have TEFs 2–3 orders of magnitude lower than the higher molecular weight PAHs, and yet the risks for a significant number of them are on the same order as the higher molecular weight

PAHs. This is because risk due to consumption of contaminated drinking water is related to the product of toxicity and aqueous solubility. For example, for the unweathered NAPL, naphthalene ranks 4th in significance while its TEF is one of the lowest, while benzo[b]fluoranthene is one of the most toxic, but its contribution to risk is negligible. This leads to an interesting point that the PAHs not on the U.S. EPA Group B2 carcinogen list but that have been assigned TEFs in the literature may actually provide a significant portion of the total risk. For these simulations, the risks for the unweathered and weathered NAPLs were 72% and 36% higher, respectively, using the Nisbet and LaGoy TEFs as compared to the U.S. EPA's TEFs. This difference is due to the contributions of the lower molecular weight PAHs not on the U.S. EPA Group B2 list that have lower TEFs but higher solubilities as compared to the higher molecular weight PAHs that are on the U.S. EPA Group B2 list. It is noteworthy that for these simulations with the weathered NAPL, 2-methylnaphthalene and anthracene both provide higher contributions to carcinogenic risks than all the group B2 carcinogens except benzo[a]pyrene. These results suggest that the U.S. EPA should consider adding TEFs for all the Priority Pollutant PAHs. Those that are not in the Group B2 carcinogen list are potentially important because of their higher solubilities.

## Discussion

The results indicate that the fraction approach is very suitable for use with PAH NAPLs. Through simulations, we showed that the model using the fraction approach was able to provide similar compositional dynamics and carcinogenic risk to the model utilizing all the PAHs, even though the two NAPLs had significantly different distributions of PAHs. Implementation of the fraction approach at a PAH NAPL site should be very straightforward. Composition data of the PAH NAPL can be determined for use with the fraction approach using established laboratory procedures (14). The only additional sample analysis necessary beyond those currently required by regulators is that which fractionates the mixture. This involves gas chromatography with a column that separates based on boiling point with subsequent subdivision of the chromatogram into EC ranges. These data then allow a very complex NAPL to be represented by a reasonable number of components equal to the sum of the number of

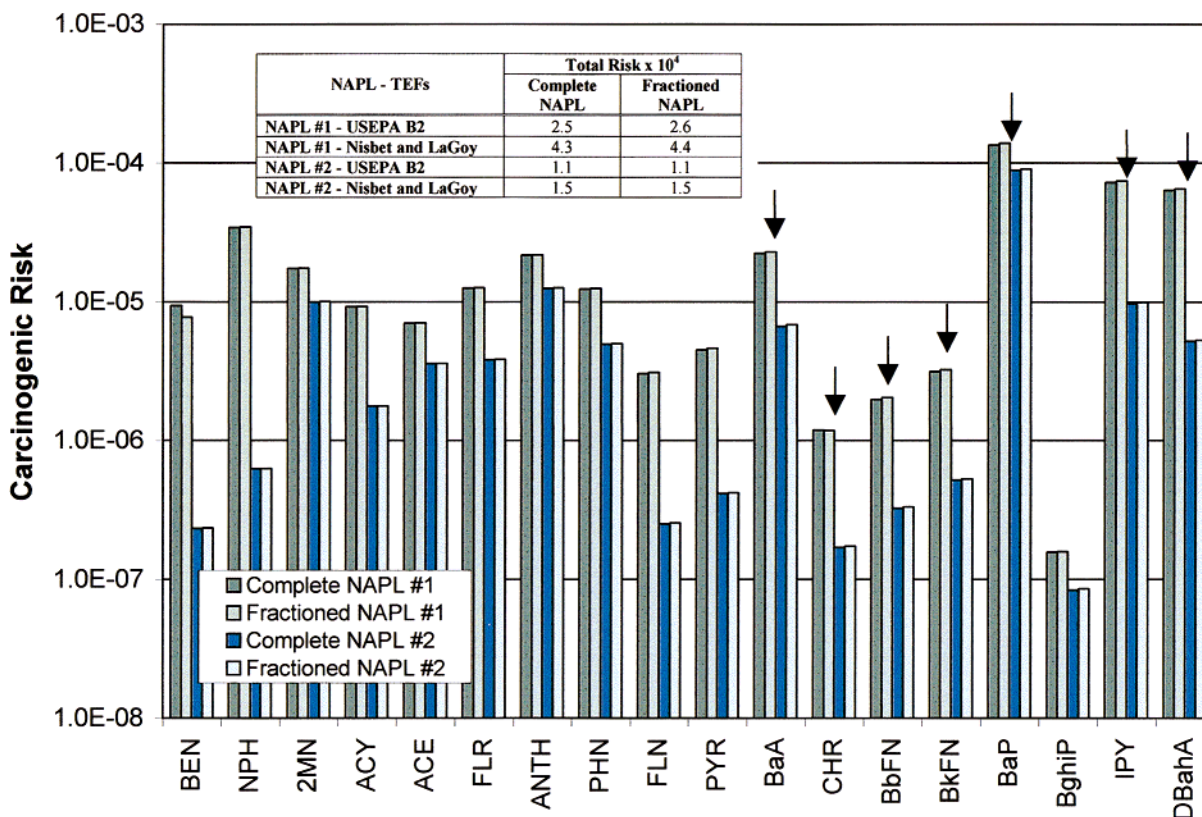


FIGURE 3. This figure shows the contribution to the total risk from the Priority Pollutants for the two NAPLs. Complete NAPL refers to the simulations that modeled all the NAPL components shown in Table 2. Fractioned NAPL refers to the simulations that modeled the NAPL using the fraction approach. The risks plotted assumed the TEF values of Nisbet and LaGoy, and the inset table shows the total risks computed using both sets of TEF values. The arrows denote the PAHs on the U.S. EPA B2 carcinogen list. These simulations show that the model using the fraction approach provides similar carcinogenic risk to the model utilizing all the compounds.

fractions required and the number of Priority Pollutants present. Thus, the fraction approach provides a convenient method for estimating risks and assessing remediation strategies at PAH NAPL sites.

The fraction approach also provides a means to improve our understanding of the true risks presented with PAH NAPL contamination, and it will facilitate selection of remediation strategies that are designed for risk reduction. Comparisons between remediation technologies can only be made by accounting for NAPL compositional changes over time, and they may provide additional information to substantiate the use of innovative technologies that might not have otherwise been chosen due to their unproven records. Indeed, the inadequacies of many current technologies are now being understood, and a recent report by the NRC focuses on requirements necessary to bring innovative technologies into the mainstream (18).

Implementation of the fraction approach has the added benefit of focusing attention on the PAHs that pose the greatest health risk, not necessarily the greatest toxicity. This is an important distinction as toxicity is only one parameter that defines the overall health risk. Risk is also a function of aqueous concentration—and in the case of PAH NAPLs, a function of the NAPL composition due to the link between NAPL mole fractions and the PAH aqueous concentrations.

The question that remains is whether the fraction approach will gain acceptance among regulators. Fortunately, the U.S. EPA, individual states, and professional organizations realize the importance of risk assessment methodologies that evaluate threats to human health and the environment and specification of remediation goals to address those threats. The U.S. EPA has stated that its goal is to conduct risk assessments on a site-by-site basis that determine the threat

level of a hazardous waste to human health and the environment and to use this risk assessment to manage risks to acceptable levels (19). Additionally, 38 states have implemented or are in the process of implementing RBCA methodologies for use at hydrocarbon-contaminated sites (20). Some states, in addition to Massachusetts, are also beginning to consider use of hydrocarbon fraction approaches in their RBCA programs. The current benchmark is the ASTM standard for RBCA at petroleum release sites (10), and the TPHCWG fraction approach can be directly implemented into the ASTM RBCA framework (9). Additionally, this approach can be implemented in future RBCA standards, such as those based on the thorough criteria outlined in a recent NRC report (21). Thus, given the benefits of utilizing the fraction approach at PAH NAPL sites and its direct applicability to RBCA, it should begin to gain acceptance among State and Federal regulators.

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