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Environmental Stability of PAH Source Indices in Pyrogenic Tars

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Polycyclic aromatic hydrocarbons (PAHs) are widespread environmental contaminants found in soil, sediments, and airborne particulates (Lima et al. 2005). While low levels of PAHs in the environment have natural origins (Wakeman et al. 1980), the majority of PAHs found in modern soils and sediments arise from myriad anthropogenic petrogenic and pyrogenic sources (Stout et al. 2004). Tars and tar products such as creosote produced from the industrial pyrolysis of coal or oil at former manufactured gas plants (MGPs) or in coking retorts are viscous, oily substances that contain significant concentrations of PAH, usually in excess of 30% w/w (Ripp et al. 1993). Thus, environmental chemists often are tasked with identifying pyrogenic tars and tar products in the environment, and distinguishing the chemical signatures of such substances from other point sources of PAHs, and/or ubiquitous anthropogenic background PAHs (Costa et al. 2004).

Combustion and pyrolysis of organic matter can yield source-specific distributions of PAH compounds (Dickhut et al. 1995; Yunker et al. 1995; Lima et al. 2005). Pyrogenic tars and tar products have unique PAH patterns (source signatures) that are a function of their industrial production (Emsbo-Mattingly et al. 2003; Costa et al. 2004). Among pyrogenic materials, certain diagnostic ratios of environmentally recalcitrant 4-, 5- and 6-ring PAHs have been identified as useful environmental markers for tracking the signature of tars and petroleum in the environment. The use of selected PAH source ratios is based on the concept that PAHs with similar properties (i.e., molecular weight, partial pressure, solubility, partition coefficients, and biotic/abiotic degradation) will weather at similar rates in the environment (Yunker et al. 1995; Costa et al. 2005) thereby yielding stable ratios. In this paper, we evaluate the stability of more than 30 high molecular weight PAH ratios during controlled studies of tar evaporation and aerobic biodegradation. The starting materials in these experiments consisted of relatively unweathered tars derived from coal and petroleum, respectively. The PAH ratios from these laboratory studies are compared to those measured in PAH residues found in tar-contaminated soils at a former MGP that operated with a carburetted water gas process.

MATERIALS AND METHODS

Samples of relatively unweathered petroleum and coal tar were obtained from the site of two manufactured gas plants and used in evaporation and aerobic biodegradation studies. Samples of seven tar-contaminated soils containing total 16 priority pollutant PAHs between 10 and 5,000 mg/kg were obtained from the site of a former carburetted water gas plant. Concentrations of PAH and alkyl PAH compounds (Table 1) were determined

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using gas chromatography/mass spectrometry in the selected ion monitoring mode that achieved reporting limits of approximately 5 µg/kg (Wang et al. 1999). PAH analytical standards were obtained from AccuStandard, Inc. (95-99% purity). Analytical quality was monitored through the use of deuterated PAH surrogates, sample duplicates, and method blanks.

A coal tar evaporation study was conduced following the methods of Douglas et al. (2002). Approximately 3 milliliters of tar was placed into separate pre-weighed 20 ml vials. The vials were placed on a temperature-regulated 40°C hot plate and purge with clean nitrogen gas at a fixed flow rate of 2 ml/min. Test vials were removed from the hot plate and, in addition to an unevaporated Control Sample, were analyzed for PAHs after 24, 48, 96, and 168 hrs of evaporation.

Table 1. Inventory of PAH compounds.[1]

#	Abbr	Compound	#	Abbr	Compound
2	N0	Naphthalene	4	FL0	Fluoranthene
2	N1	C1-Naphthalenes	4	PY0	Pyrene
2	N2	C2-Naphthalenes	4	FP1	C1-Fluoranthenes/Pyrenes
2	N3	C3-Naphthalenes	4	FP2	C2-Fluoranthenes/Pyrenes
2	N4	C4-Naphthalenes	4	FP3	C3-Fluoranthenes/Pyrenes
2	B	Biphenyl	4	FP4	C4-Fluoranthenes/Pyrenes
3	DF	Dibenzofuran	4	NBT0	Naphthobenzothiophenes
3	AY	Acenaphthylene	4	NBT1	C1-Naphthobenzothiophenes
3	AE	Acenaphthene	4	NBT2	C2-Naphthobenzothiophenes
3	F0	Fluorene	4	NBT3	C3-Naphthobenzothiophenes
3	F1	C1-Fluorenes	4	NBT4	C4-Naphthobenzothiophenes
3	F2	C2-Fluorenes	4	BA0	Benz[a]anthracene
3	F3	C3-Fluorenes	4	C0	Chrysene/Triphenylene
3	A0	Anthracene	4	BC1	C1-Chrysenes
3	P0	Phenanthrene	4	BC2	C2-Chrysenes
3	PA1	C1-Phenanthrenes/Anthracenes	4	BC3	C3-Chrysenes
3	PA2	C2-Phenanthrenes/Anthracenes	4	BC4	C4-Chrysenes
3	PA3	C3-Phenanthrenes/Anthracenes	5	BB	Benzo[b]fluoranthene
3	PA4	C4-Phenanthrenes/Anthracenes	5	BJK	Benzo[k]fluoranthene
3	RET	Retene	5	BB	Benzo[a]fluoranthene
3	DBT0	Dibenzothiophene	5	BEP	Benzo[e]pyrene
3	DBT1	C1-Dibenzothiophenes	5	BAP	Benzo[a]pyrene
3	DBT2	C2-Dibenzothiophenes	5	PER	Perylene
3	DBT3	C3-Dibenzothiophenes	5	DA	Dibenz[a,h]anthracene
3	DBT4	C4-Dibenzothiophenes	6	IND	Indeno[1,2,3-cd]pyrene
4	BF	Benzo(b)fluorene	6	GHI	Benzo[g,h,i]perylene

[1] number of rings in each compound identified in '#' column

A petroleum tar aerobic biodegradation experiment was conducted following the generalized methods of Allen-King et al. (1994). Using antiseptic techniques, approximately 5 µg of petroleum tar was added to a series of headspace-free 10-ml test vials, to which was added sterile 15% Bushnell-Haas nutrient solution. This mixture was further amended with 1 ml of a bacterial inoculant that contained approximately 6 x 10^8 cells/ml of hydrocarbon degrading bacteria that had been cultured from ambient soil (Cytoculture, Inc.). All the test bottles were gently agitated at approximately 30°C. Separate test vials were sacrificed after 4 and 7 weeks of exposure by adding 3 ml of

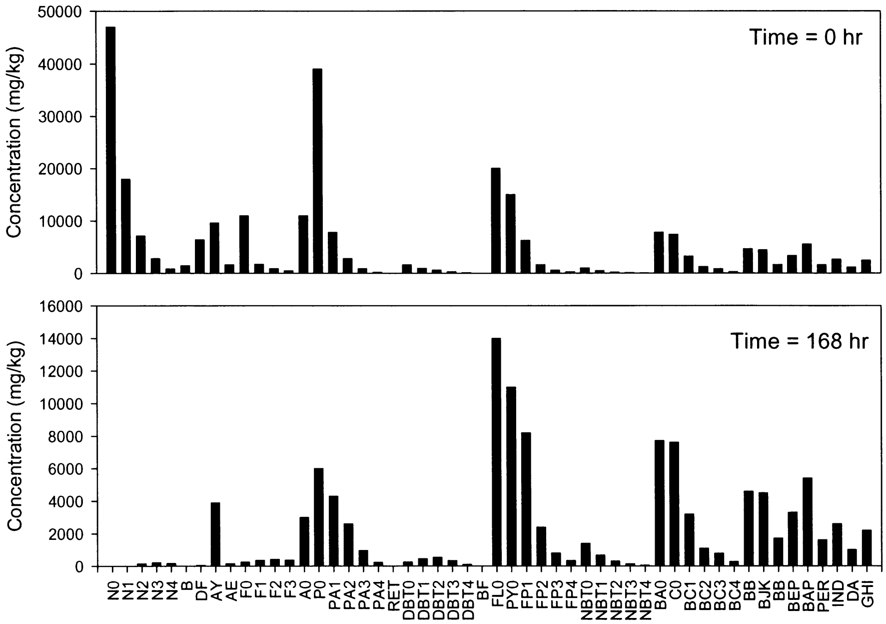

Figure 1. Change in PAH composition of coal tar in laboratory evaporation study.

methylene chloride to the mixture. Control Samples were run concurrent with the experiment to document antiseptic control and lack of abiotic removal of tar PAHs during the course of the experiment.

RESULTS AND DISCUSSION

The results of the coal tar evaporation study are presented in Table 2. Here, a variety of 2-, 3-, 4-, 5- and 6-ring PAH indices are presented for the Control Sample (T=0) and the series of progressively evaporated tars. The extent of evaporation was measured relative to the weathering index of Costa et al. (2005), expressed as the sum of the 2- and 3- ring priority pollutant PAHs divided by the sum of the 4-, 5-, and 6- ring priority pollutant PAHs. The extent of evaporation was gauged relative to the loss of PAHs over the course of the experiment. Progressive loss of PAHs was noted, culminating in a heavily weathered tar analog at the termination of the experiment (Figure 1). The stability of a given index relative to evaporative weathering was measured as the percent change (% Chg) between that measured in the Control Sample and that for the most highly evaporated sample (T=168). Operationally, we interpret a % Chg of less than 15% in a particular index as stable, and greater than 15% different as unstable relative to evaporative weathering.

Certain PAH indices were unstable relative to evaporative weathering, including most of the more volatile 2- and 3-ring PAH, e.g., N0/(N2+N3), DF/F0, (P0+A0)/(PA2+PA3), DBT0/(DBT2+DBT3), ($\sum$DBT0-DBT4)/(BA0+C0). Similarly, some 4-ring indices also showed significant variability due to evaporation, e.g., (FL0+PY0)/(FP2+FP3), BC1/FP1 and the naphthobenzothiophene (NBT) series. Importantly, certain 3-ring PAH indices (DBT2/PA2, DBT3/PA3) many 4-ring, and all of the 5- and 6-ring indices were stable relative to evaporative weathering.

Table 2. Stability of selected PAH indices from a coal tar evaporation study.

PAH Index	T=0 h	T=24 h	T=48 h	T=96 h	T=168 h	% Chg
Weathering Index	1.68	0.46	0.34	0.30	0.22	-
N0/(N2+N3)	4.747	0.042	0.088	0.055	0.020	100%
DF/F0	0.582	0.207	0.256	0.233	0.173	70%
DB2/PA2	0.221	0.217	0.206	0.213	0.208	6%
DB3/PA3	0.361	0.350	0.336	0.345	0.354	2%
(P0+A0)/(PA2+PA3)	13.77	5.667	4.136	3.643	2.528	82%
DBT0/(DBT2+DBT3)	1.739	0.783	0.600	0.500	0.295	83%
(∑DBT0-DBT4)/(BA0+C0)	0.232	0.201	0.162	0.148	0.112	52%
BF/FP1	0.199	0.199	0.201	0.210	0.208	-5%
BA0/(BA0+C0)	0.513	0.513	0.506	0.506	0.503	2%
FL0/(FL0+PY0)	0.571	0.571	0.563	0.552	0.560	2%
Fl0/PY0	1.333	1.333	1.286	1.231	1.273	5%
BA0/C0	1.054	1.052	1.026	1.026	1.013	4%
C0/(C0+FP1)	0.544	0.458	0.467	0.473	0.481	12%
BC1/FP1	0.516	0.352	0.364	0.379	0.390	24%
(FL0+PY0)/(FP2+FP3)	16.20	10.836	9.846	8.951	7.813	52%
(BA0+C0)/(BC2+BC3)	7.677	7.861	8.387	8.449	8.095	-5%
NBT0/C0	0.128	0.182	0.182	0.179	0.184	-43%
NBT2/BC2	0.158	0.250	0.264	0.273	0.273	-72%
NBT3/BC3	0.112	0.160	0.171	0.169	0.177	-59%
NBT0/BAP	0.173	0.246	0.259	0.255	0.259	-50%
NBT2/BAP	0.035	0.053	0.054	0.055	0.056	-61%
NBT3/BAP	0.016	0.023	0.024	0.024	0.026	-64%
BEP/BAP	0.600	0.614	0.611	0.618	0.611	-2%
BBF/BAP	0.836	0.825	0.833	0.818	0.852	-2%
BKF/BAP	0.800	0.825	0.852	0.873	0.833	-4%
(BBF+BKF)/BAP	1.636	1.649	1.685	1.691	1.685	-3%
BBF/BKF	1.045	1.000	0.978	0.938	1.022	2%
PER/BAP	0.291	0.281	0.296	0.291	0.296	-2%
(BBF+BKF)/C0	1.216	1.221	1.182	1.192	1.197	2%
PER/C0	0.216	0.208	0.208	0.205	0.211	3%
IP/(IP+GHI)	0.520	0.538	0.531	0.542	0.542	-4%
IP/GHI	1.083	1.167	1.130	1.182	1.182	-9%

The results of the aerobic biodegradation study are presented in Table 3. PAH indices based on 2-, 3-, 4-, 5- and 6-ring PAH compounds are presented for the Control Sample (BD-C) and the tars exposed to aerobic bacteria for 4 weeks and 7 weeks, respectively. The extent of biodegradation was measured relative to the weathering index of Costa et al. (2005). The extent of biodegradation was evaluated relative to the loss of PAHs over the course of the experiment. Progressive temporal loss of PAHs was noted, culminating in a severely weathered tar analog at the termination of the experiment (Figure 2).

Generally, the stability of the PAH indices measured in the biodegradation experiment paralleled those observed in the evaporation study (Table 2). Unstable indices included the lower molecular weight 2- and 3-ring PAH, e.g., N0/(N2+N3), DF/F0,

Table 3. Stability of selected PAH indices from a carburetted water gas tar aerobic biodegradation study.

Parameter	BD-C T=0	BD-4 T= 4 wks	BD-7 T=7 wks	% Chg
Weathering	2.05	0.05	0.06	-
N0/(N2+N3)	14.0	0.010	0.011	100%
DF/F0	0.165	0.667	0.506	-206%
DB2/PA2	0.272	0.277	0.291	-7%
DB3/PA3	0.420	0.417	0.433	-3%
(P0+A0)/(PA2+PA3)	13.571	0.286	0.370	97%
DBT0/(DBT2+DBT3)	3.101	0.068	0.073	98%
(∑ DBT0-DBT4)/(BA0+C0)	0.506	0.144	0.140	72%
BF/FP1	0.088	0.092	0.087	1%
BA0/(BA0+C0)	0.474	0.468	0.460	3%
FL0/(FL0+PY0)	0.424	0.397	0.394	7%
Fl0/PY0	0.735	0.658	0.650	12%
BA0/C0	0.901	0.878	0.852	5%
C0/(C0+FP1)	0.490	0.477	0.489	0.2%
BC1/FP1	0.243	0.211	0.217	11%
(FL0+PY0)/(FP2+FP3)	30.256	26.033	27.500	9%
(BA0+C0)/(BC2+BC3)	20.149	21.096	22.958	-14%
NBT0/C0	0.211	0.232	0.227	-8%
NBT2/BC2	0.271	0.302	0.327	-21%
NBT3/BC3	0.947	1.100	1.211	-28%
NBT0/BAP	0.169	0.194	0.200	-19%
NBT2/BAP	0.015	0.016	0.017	-16%
NBT3/BAP	0.020	0.022	0.023	-14%
BEP/BAP	0.618	0.622	0.640	-4%
BBF/BAP	0.584	0.551	0.560	4%
BKF/BAP	0.483	0.490	0.500	-3%
(BBF+BKF)/BAP	1.067	1.041	1.060	1%
BBF/BKF	1.209	1.125	1.120	7%
PER/BAP	0.236	0.235	0.240	-2%
(BBF+BKF)/C0	1.338	1.244	1.205	10%
PER/C0	0.296	0.280	0.273	8%
IP/(IP+GHI)	0.474	0.477	0.474	-0.1%
IP/GHI	0.900	0.910	0.901	-0.1%

(P0+A0)/(PA2+PA3), DBT0/(DBT2+DBT3), (∑DBT0-DBT4)/(BA0+C0). The 4-ring naphthobenzothiophene (NBT)-based indices also showed significant variability due to biodegradation. The stable indices included selected 3-ring PAH indices (DBT2/PA2, DBT3/PA3), several 4-ring, and all of the 5- and 6-ring indices. It is interesting to note that while there was general agreement in the trends of index stability between the evaporation and biodegradation studies, there were, in fact, some differences in the relative stabilities of many of the indices. We attribute these differences to those imparted by a strictly physical process (evaporation) versus those that result from more complex biotic degradation mechanisms. We conclude that those indices stable to the effects of evaporative and biodegradation are suitable candidates for PAH source identification in environmental investigations.

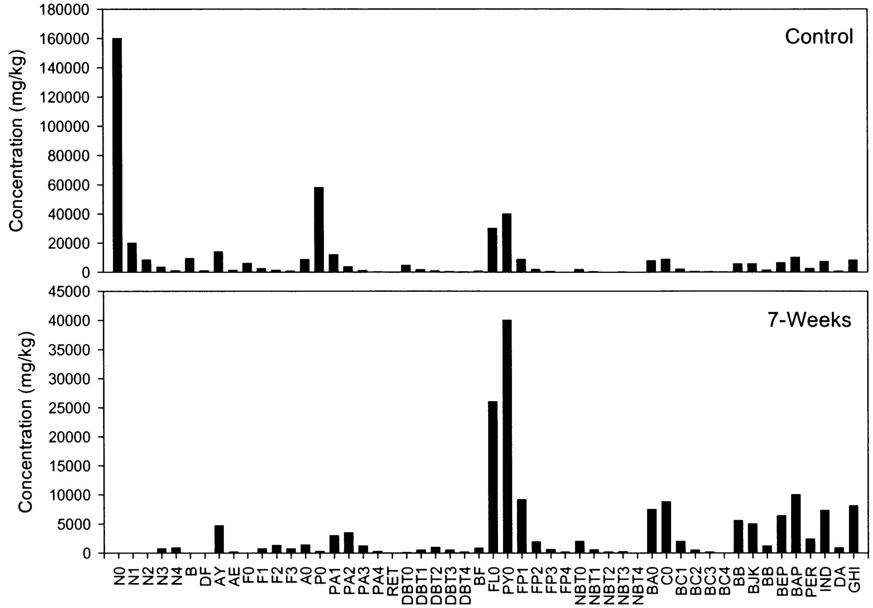

Figure 2. Change in PAH composition of carburetted water gas tar during course of laboratory aerobic biodegradation study.

The apparent stability of selected PAH indices was evaluated in seven field soils from a former MGP that contain residues of carburetted water gas tar. The concentration of tar residues in these samples ranged from 10 to 5,000 mg/kg. The weathering state, per Costa et al. (2005) ranged from 1.82 (relatively unweathered) to 0.35 (highly weathered). The mean, standard deviation, and percent coefficient of variation (%CV) in selected PAH indices measured in these samples is presented in Table 4. On one hand, the stability of many of the 4-, 5- and 6-ring pyrogenic PAHs was found to be remarkably stable, and suitable for source identification (e.g., BF/FP1, BA0/(BA0+C0), FL0/(FL0+PY0), FL0/PY0, BA0/C0, BEP/BAP, BBF/BAP, BKF/BAP, (BBF+BKF)/BAP, BBF/BKF, PER/BAP, (BBF+BKF)/C0, PER/C0, IP/(IP+GHI), IP/GHI). However, certain indices—particularly those attributable to petrogenicity (e.g., DB2/PA2, DB3/PA3, (FL0+PY0)/(FP2+FP3), (BA0+C0)/(BC2+BC3)) rather than pyrogenicity—showed significantly more variability among the field samples than observed in the laboratory evaporation and biodegradation experiments. We attribute this variability to changes in the petroleum feedstock that produced the carburetted water gas tar at the site over time. Importantly, the pyrogenic features of the tar, largely expressed in the unsubstituted 4-, 5-, and 6-ring PAH ratios, remained consistent.

The results of this work provides evidence, consistent with the literature, that PAH compounds and isomers of similar structure and physical chemistry behave similarly in the environment, and that ratios of such compounds remain stable across a wide range of weathering and concentration. Such indices are suitable markers for tracking the fate of PAH-containing materials in soils and sediments.

Table 4. Variability of selected PAH indices in tar-containing soil samples from a carburetted water gas plant site (n=7 samples).

Parameter	Mean	Std Dev	%CV
N0/(N2+N3)	1.807	1.995	110%
DF/F0	0.125	0.052	41%
DB2/PA2	0.312	0.116	37%
DB3/PA3	0.622	0.341	55%
(P0+A0)/(PA2+PA3)	7.184	4.455	62%
DBT0/(DBT2+DBT3)	1.033	0.510	49%
(∑DBT0-DBT4)/(BA0+C0)	0.559	0.451	81%
BF/FP1	0.097	0.011	11%
BA0/(BA0+C0)	0.515	0.009	2%
FL0/(FL0+PY0)	0.400	0.011	3%
Fl0/PY0	0.666	0.031	5%
BA0/C0	1.064	0.037	3%
C0/(C0+FP1)	0.399	0.069	17%
BC1/FP1	0.375	0.082	22%
(FL0+PY0)/(FP2+FP3)	9.770	4.528	46%
(BA0+C0)/(BC2+BC3)	7.193	2.503	35%
NBT0/C0	0.216	0.072	33%
NBT2/BC2	0.315	0.129	41%
NBT3/BC3	0.344	0.068	20%
NBT0/BAP	0.237	0.085	36%
NB2/BAP	0.094	0.095	101%
NB3/BAP	0.048	0.050	106%
BEP/BAP	0.572	0.043	8%
BBF/BAP	0.509	0.044	9%
BKF/BAP	0.565	0.047	8%
(BBF+BKF)/BAP	1.074	0.074	7%
BBF/BKF	0.904	0.087	10%
PER/BAP	0.167	0.014	8%
(BBF+BKF)/C0	0.989	0.109	11%
PER/C0	0.154	0.016	11%
IP/(IP+GHI)	0.486	0.017	3%
IP/GHI	0.948	0.063	7%

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