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Phenols and Hydroxy-PAHs (Arylphenols) as Tracers for Coal Smoke Particulate Matter: Source Tests and Ambient Aerosol Assessments

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Source tests were conducted to analyze and characterize diagnostic key tracers for emissions from burning of coals with various ranks. Ambient aerosol particulate matter was also collected in three areas of China and a background area in Corvallis, OR (U.S.) to confirm the presence of tracers specific for coal smoke. The results showed a series of aliphatic and aromatic hydrocarbons and phenolic compounds, including PAHs and hydroxy-PAHs as the major tracers, as well as a significant unresolved complex mixture (UCM) of compounds. The tracers that were found characteristic of coal combustion processes included hydroxy-PAHs and PAHs. Atmospheric ambient samples from Beijing and Taiyuan, cities where coal is burned in northern China, revealed that the hydroxy-PAH tracers were present during the wintertime, but not in cities where coal is not commonly used (e.g., Guangzhou, South China). Thus, the mass of hydroxy-PAHs can be apportioned to coal smoke and the source strength modeled by summing the proportional contents of EC (elemental carbon), PAHs, UCM and alkanes with the hydroxy-PAHs.

Introduction

The burning of coal as a fuel has been shown to significantly increase the input of particulate organic aerosol components to the atmosphere. As a source of smoke emissions, or in conjunction with other particle emissions, it influences atmospheric chemical, optical, and radiative properties. These changes occur through direct (adsorption and scattering of solar and terrestrial radiation) and indirect (modification of cloud processes) mechanisms (*1*). The composition and source strength of coal burning emissions are important for understanding that organic input to atmospheric chemistry and will complement existing data on the characterization of organic emissions from burning of biomass (*2*−*8*), of plastics (*9*), and of fossil fuels such as petroleum products (*10*, *11*) as well as some coals (*12*−*15*). Such compositional data are necessary for atmospheric source apportionment studies (e.g., refs *16*−*18*).

Coal Rank. Coal rank is a scale of the geological maturity of coals. During the geological coalification processes, plant remains undergo a sequence of physical, biochemical and chemical changes (diagenesis, then catagenesis) which result in a series of coals of increasing rank or maturity (*19*, *20*). The coal ranks with the progression of maturity are peat → lignite → semibituminous → bituminous → anthracite (*21*). The sequence of chemical reactions associated with coalification is: dehydration, loss of oxygen containing functional groups, alkylation, and oligomerization (*21*). The degree of completion of these chemical reactions within the depositional environment determines the general structure of coals (*20*, *21*). As coal maturity increases, the degree of aromaticity increases and the number of aliphatic linkages or bridges decreases. Thus, the emissions of aliphatic versus aromatic products from burning of coals are highly dependent on their rank as well as combustion conditions.

The identification of combustion products may be utilized as a chemical fingerprint for identifying source inputs, transport mechanisms, and receptor fate in samples of atmospheric fine particulate matter (PM). Coal smoke and other source emissions (e.g., petroleum product use) introduce airborne fine PM containing polycyclic aromatic hydrocarbons (PAHs), which have mutagenic and genotoxic potential (*22*, *23*). However, PAHs are nonspecific source tracers because they are emitted from any combustion/burning process, as well as directly by fuel spillage. Thus, the aim of this study is to report new organic tracers for smoke particulate matter emitted by flaming and smoldering combustion of lignite, bituminous coals, and anthracite from China, Europe, and the U.S. In this case, the directly emitted and thermally altered molecular tracers may be used specifically for tracking coal smoke emissions in the environment, which will be demonstrated for aerosol PM from China.

Experimental Methods

Sampling. Coal samples ranging in rank from lignite to anthracite were collected and burned in two sets of experiments (Table 1). Sample set 1 included two lignites, a semibituminous and a bituminous coal. These coal samples were burned at Oregon State University using an open, controlled fire under both flaming (active fire flame) and smoldering (glowing embers, no flame) conditions. The emitted smoke was collected on an organically clean quartz fiber filter (annealed at 550 °C for 3 h; 100% particle size retention >2.0 μm, i.e., TSP) using a high volume air sampler located approximately 1.5 m diagonally above and to the side of the flames in the smoke plume. Smoke was sampled for approximately 10 min at a suction flow rate of 1.13 m^3/min. After sampling, a portion of each filter (8.8 cm^2) was cut out and set aside for volatile organic carbon (OC) and elemental carbon (EC) analysis (*24*). The collection filters were then placed in precleaned 300 mL jars with Teflon lined lids to which 10 mL of dichloromethane was added. The jars

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TABLE 1. Coal Samples Burned for Source Tracer Tests and Elemental Carbon Emission Factors

sample (code)	coal name, mine area	coal rank	EC emission (g/kg coal burned)
set 1[a]			
Fortuna (FL)	lignite, Fortuna Mine, Germany	lignite	0.17
Leuna (LB)	Braunkohle, Leuna, Thüringen, Germany	lignite	0.21
Kayenta (KW)	Kayenta Wepo Formation, Black Mesa, AZ	semibituminous	0.47
Wales (UK)	Wales coal, UK	bituminous	1.38
set 2[b]			
Datong (DT)	Datong, Shanxi, China	semibituminous	10.12
Xin-An (XA)	Xinan, Henan, China	bituminous	6.97
An-Yang (AY)	Anyang, Henan, China	anthracite	0.002

[a] Data from Oros and Simoneit (*12*). [b] Data from Chen et al. (*14*).

were stored at 4 °C until chemical extraction was conducted.

The coal samples (honeycomb briquettes) of set 2 were burned for source tests in a briquette stove in China, and the emitted smoke was collected as TSP on quartz fiber filters as described in Chen et al. (*14*). Three samples (semibituminous, bituminous, and anthracite) from that set were analyzed. It is assumed that the molecular compositions of the smoke from the same coal ranks of the two sets of experiments are the same. However, the compound concentrations for the stove tests are drastically lower due to the greater combustion efficiency.

Ambient Aerosol Particles. Aerosol PM was collected during winter as total suspended particles (TSP) in Guangzhou and Taiyuan (Shanxi), and as PM10 in Beijing, China, with either glass or quartz fiber filters (20 × 25 cm). Acquisition was with a high-volume air sampler for 24 h each. The detailed data for the Guangzhou and Beijing aerosol sampling programs are presented elsewhere (*25*). The reference aerosol from Corvallis, Oregon was taken as TSP in late fall under a strong influence from wood burning emissions (coal is not used as a fuel).

Extraction and Concentration. Each filter was extracted using ultrasonic agitation for three 20 min periods using 200 mL of dichloromethane (CH_2Cl_2, nannograde, glass distilled). The solvent extract was filtered using a Gelman Swinney filtration unit containing an annealed glass fiber filter for the removal of insoluble particles. The filtrate was first concentrated by use of a rotary evaporator and then a stream of filtered nitrogen gas. The final volume was adjusted to exactly 4.0 mL by addition of CH_2Cl_2. Aliquots (20 μL) were taken for conversion to the trimethylsilyl (TMS) derivatives. The reaction of the extract aliquot with N,O-bis-(trimethylsilyl)trifluoroacetamide (BSTFA, 20 μL) plus 1% trimethylchlorosilane and pyridine (5 μL) was carried out for approximately 3 h at 70 °C prior to analysis. This transforms alcohol and phenol hydroxyls to TMS ethers and alkanoic acids to TMS esters.

Instrumental Analyses. Both total extracts and silylated total extracts were analyzed by gas chromatography-mass spectrometry (GC-MS) using a Hewlett-Packard model 5973 MSD quadrupole mass spectrometer operated in the electron impact mode at 70 eV, with an ion source temperature of 230 °C, and coupled to a Hewlett-Packard model 6890 gas chromatograph. The GC was equipped with a 30 m × 0.25 mm i.d. capillary column coated with DB-5MS (Agilent, film thickness 0.25 μm) and using He as carrier gas at a flow rate of 1.2 mL/min. The GC temperature program was: injector at 280 °C, oven at 2 min isothermal hold at 65 °C, ramp to 300 °C at 6 °C/min, and isothermal hold at 300 °C for 20 min.

Compound Identification and Quantification. Compound identifications are based on comparisons with authentic standards, GC retention time, literature mass spectra and interpretation of mass spectrometric fragmentation patterns. Quantification of the compounds was conducted by comparison of GC-MS peak area with that of coinjected or external standards (e.g., naphthol, perdeuterated tetracosane). Compound response factors were determined by GC-MS of standards with known concentrations. Emission factors were determined from gravimetric weight measurements of the fuel sample before and after burning (dry ash). The following standards were purchased: 1- and 2-naphthol, 9-phenanthrol, and 2-hydroxyfluorene from Aldrich Chemical Co.; 9-hydroxyfluorene and 1-hydroxypyrene from Arcos Chemical Company; 6-hydroxychrysene from AccuStandard Company, and 3-hydroxybenzo[a]pyrene from Fluka Chemical Company.

The predominant particle-associated hydroxy-PAHs in coal smoke are hydroxyphenanthrenes/anthracenes (molecular weight, MW 194), hydroxyfluoranthenes/pyrenes (MW 218), and hydroxybenzanthracenes/chrysenes (MW 244), with their respective monomethyl homologs. The more volatile naphthols, methylnaphthols, hydroxyfluorenes, and hydroxymethylfluorenes are also significant in coal smoke particles and may be detectable in atmospheric samples closer to such source emissions.

Results and Discussion

Coal Burning Source Tests. Table 1 provides a summary of the types of coals tested and their characteristics. The organic compounds identified in the solvent soluble fraction of coal smoke particles from set 1 of 2 test series have been reported with their emission factors and percent abundances (*12*). Hydroxy-PAHs (arylphenols) were not reported. The distributions of the molecular classes found included the following: homologous series of *n*-alkanes, *n*-alkenes, *n*-alkan-2-ones, *n*-alkanals, *n*-alkanoic acids, *n*-alkenoic acids, *n*-alkanols, *n*-alkylbenzenes, and *n*-alkylnitriles; PAHs; phenols; UCM (unresolved complex mixture of branched and cyclic compounds); hopanoid, steroid, and terpenoid molecular biomarkers, as well as the OC and EC data. The distributions and abundances of the coal smoke constituents were strongly dependent on coal rank and on combustion duration and temperature (smoldering versus flaming conditions) (*12*).

Some of those values reported as detailed below and coupled with the proposed new tracers presented here are useful as relative chemical fingerprints for smoke from coal burning in urban atmospheres. The following compounds and homologous compound series were selected to be the representative tracers and mass emission factors from coal smoke: *n*-alkanes, UCM, selected hopanes, phenols, PAHs, and the hydroxy-PAHs. These compounds are summarized in Table 2 as mass emission factors and are discussed in more detail below.

A typical GC-MS total ion current trace for the total extract of coal smoke particulate matter is shown in Figure 1a, and the related data are given in the Supporting Information (SI) Figures SI-1 and SI-2. The major signal is due to the UCM and the dominant resolved compounds are the PAHs and

TABLE 2. Emission Factors (mg/kg of Coal Burned) of the Key Tracers from Burning of Coals in Open Fires and Briquette Stoves

	coal smoke[a]						
compound	Fortuna Lignite (FL)	Leuna Brown (LB)	Kayenta semibituminous (KW)	Wales bituminous (UK)	Datong semibituminous (DT)[b]	Xin-An bituminous (XA)[b]	An-Yang anthracite (AY)[b]
alkanes							
total	7422	1344	13516	1705	4.76	0.55	0.14
CPI	1.26	1.15	1.04	1.02	1.00	0.90	0.91
Cmax	29	30	27	24	22	21	24
hopanes							
17α(H)-22,29,30-trisnorhopene	325	12	150	17	0.03		
17α(H)-22,29,30-trisnorhopane	195	10	430	67	0.04		0.01
17β(H)-22,29,30-trisnorhopane	442	15	492	23	0.02		0.03
17α(H),21β(H)-29-norhopane	56	19	656	85	0.07		0.01
17β(H),21α(H)-29-norhopane	566	7	729	43	0.04		<0.01
17α(H),21β(H)-hopane	97	10	335	45	0.04		0.03
17β(H),21α(H)-hopane	1111	6	473	42	0.04		0.01
22S-17α(H),21β(H)-Homohopane	49	1	170	10	0.01		<0.01
22R-17α(H),21β(H)-homohopane	840	12	160	17	0.01		<0.01
17β(H),21α(H)-homohopane	195	5	170	19	0.01		
S-17α(H),21β(H)-bishomohopane			100			0.00	
R-17α(H),21β(H)-bishomohopane			90			0.00	
17β(H),21α(H)-bishomohopane						0.00	
total	3876	97	3955	368	0.32		0.09
PAHs							
fluorene	26	8	15	24	0.01	0.01	
methylfluorenes	68	14	98	70	0.03	0.03	
dimethylfluorenes	62	10	43	58	0.06	0.08	
phenanthrene (Phe)	129	31	152	239	0.46	0.21	<0.001
anthracene (Ant)	20	6	85	105	0.38	0.07	<0.001
methylphenanthrenes	224	89	767	571	1.95	0.60	<0.001
3-methylphenanthrene	30	12	92	83	0.26	0.15	
2-methylphenanthrene	44	17	151	90	0.44	0.16	
9-methylanthracene	20	7	129	111	0.29	0.06	
9-methylphenanthrene	38	14	86	124	0.48	0.13	
1-methylphenanthrene	92	39	309	163	0.47	0.10	
C_2−178	174	75	1773	843	0.67	0.52	<0.001
fluoranthene (Fl)	40	32	323	614	1.20	0.72	0.003
acephenanthrylene	7	15	193	300	0.46	0.32	0.001
pyrene (Py)	47	29	355	561	1.10	0.64	0.002
C_1−202	128	37	783	610	1.37	0.68	0.004
C_2−202			178		0.48	0.57	0.002
retene	101	47	282	20	2.45		
benzo[ghi]fluoranthene		2	58	24	0.38	0.15	0.001
cyclopenta[cd]pyrene			27	170	0.57	0.07	<0.001
benz[a]anthracene (BaA)	10	17	100	324	0.65	0.37	0.003
chrysene (Chry)	14	18	82	303	0.77	0.30	0.006
C_1−228		18	878	372	0.36	0.53	0.005
C_2−228		26	367	120	0.25	0.25	0.001
benzo[b+k]fluoranthenes		12	160	730	0.77	0.35	0.016
benzo[a]fluoranthene		2	28	86	0.19	0.06	
benzo[a]pyrene (BaP)		4	53	194	0.38	0.20	0.001
benzo[e]pyrene (BeP)		2	51	253	0.22	0.26	0.014
perylene		1	26	40	0.08		
C_1−252			62	186	0.58	0.68	
C_2−252					0.17	0.38	0.017
indeno[1,2,3,4-cdef]chrysene					0.08	0.04	0.009
indeno[cd]pyrene (IcdP)				158	0.18	0.09	0.005
benzo[ghi]perylene (BghiP)			18	291	0.10	0.09	0.009
dibenz[ah]anthracene				7	0.04	0.05	0.003
picene				94	0.05	0.04	0.005
C_1−278				41	0.01	0.08	0.001
total	1274	584	7724	7979	18.39	9.03	0.11
Phe/(Phe+Ant)	0.87	0.84	0.64	0.69	0.55	0.75	0.42
Fl/(Fl+Py)	0.46	0.52	0.48	0.52	0.52	0.54	0.54
BaA/(BaA+Chry)	0.42	0.49	0.55	0.52	0.46	0.55	0.32
BeP/(BeP+BaP)		0.33	0.49	0.57	0.37	0.57	0.95
IcdP/(IcdP+BghiP)			0.31	0.35	0.64	0.51	0.37

phenols. It should be noted that the source tests of the coals in set 1 (open burning) yield extremely high emission factors compared to the stove burn tests with briquettes (set 2). Thus, the compounds emitted in set 1 are utilized as characteristic indicators for coal smoke and the concentrations of these compounds from set 2 (Table 2) are used to apportion their ambient contribution to the total aerosol burden in China.

The hopane biomarkers and their source implications have been discussed in more detail elsewhere (*12*, *13*, *26*).

TABLE 2. Continued.

compound	Fortuna Lignite (FL)	Leuna Brown (LB)	Kayenta semibituminous (KW)	Wales bituminous (UK)	Datong semibituminous (DT)[b]	Xin-An bituminous (XA)[b]	An-Yang anthracite (AY)[b]
	coal smoke[a]						
hydroxy-PAHs							
naphthols	40	12	7.4	270	0.71	0.14	$<$0.001
methylnaphthols	105	28	18	534	1.60	0.12	$<$0.001
dimethylnaphthols	64	15	12	443	1.40	0.06	
hydroxyfluorenes	26	3	8	210	0.80	0.16	$<$0.001
C_1−182	51		5	160	2.00	0.39	$<$0.001
C_2−182	32		3	110	1.38	0.25	
phenanthrols (OH-Phe)+anthrols	47	18	224	159	4.10	0.41	$<$0.001
C_1−194	8	12	206	132	3.85	0.25	
hydroxypyrenes+fluoranthenes	13	4	88	43	2.02	0.38	$<$0.001
C_1−218	15		76	22	4.27	0.55	
hydroxychrysenes (OH-Chry)+ benzanthrols	3	2	45	40	1.08	0.27	
hydroxybenzo[a/e]pyrenes (OH−BaP)	1		40		0.66	0.18	
total	405	94	732	2123	23.87	3.16	$<$0.01
Phe/OH-Phe	3.17	2.10	1.06	2.16	0.20	0.68	0.12
Py/OH-Py	7.23	19.00	9.90	34.30	1.36	4.42	1.99
chry/OH-Chry	8.00	17.50	4.04	15.68	1.31	2.48	9.92
BaP/OH−BaP			6.80		2.36	4.83	
total all compounds (no UCM)	12977	2119	25927	12175	47.33	12.74	0.33
UCM[c]	96000	73000	40000	24000	83	35	0.2

[a] Smoke samples for FL, LB, KW, and UK were from open fire tests and for DT, XA, and AY from stove tests burning briquettes as reported by Chen et al. (*14*). [b] These compounds are part of the complete composition listing reported by Bi et al. (*15*), but given here as mg/kg of coal burned, not as ìg/g of total smoke particles. [c] UCM = unresolved complex mixture.

Hopanes were detected in our analyses (Table 2). They have multiple emission sources such as petroleum utilization by vehicular traffic, burning of coal fuels, and biomass burning of detrital organic matter (e.g., agricultural and forestry wastes). Thus, these compounds are not source specific but contribute to the total mass emission of each source.

PAHs. *Parent PAHs.* Polycyclic aromatic hydrocarbons (as the parent PAHs) were present in coal smoke as abundant constituents comparable to the *n*-alkanes (Table 2, Figure 1a). PAHs are derived from the high temperature thermal alteration of coal organic matter and are, therefore, not as dominant in the unburned coals. The major PAHs are unsubstituted with significant methyl and dimethyl PAH homologs. The high abundances of these compounds in coal smoke reflect the degree of aromaticity and $Ar-CH_2-Ar$ linkages (i.e., rank) in the coal fuels. Molecular markers from natural triterpenoids such as picene and alkylpicenes are only trace components (*27*). The total emission factors for PAHs in all coal smoke samples range from 0.1 to 7980 mg/kg (Table 2) and are dependent on rank and style of burning. Generally, as maturity increases, the degree of aromaticity increases. The smoke from coal with maturity around $R_0 =$ 1.0% (semibituminous) showed the highest level of PAHs, which is consistent with other studies (*28*, *29*). The high emission rates of PAHs from open burning and from honeycomb coal briquette combustion (Table 2) confirmed that coal burning is a major contributor of PAHs to the atmosphere.

Diagnostic ratios for PAHs, such as Phe/(Phe+Ant), BaA/(BaA+Chry), and IcdP/(IcdP+BghiP), have been proposed to model PAH origin in ambient aerosols; for example, in Chicago, IL (*30*). The PAHs were modeled to originate from traffic and industry (steel and coke plants) based on concentration profiles and correction for decay rates of the reactive compounds (*30*). The average ratios of Phe/(Phe+Ant), Fl/(Fl+Py), BaA/(BaA+Chry), BeP/(BeP+BaP), and IcdP/(IcdP+BghiP) for these coal smoke samples were 0.68 ± 0.14, 0.51 ± 0.03, 0.47 ± 0.08, 0.55 ± 0.18, and 0.44 ± 0.14, respectively (Table SI-1). No relationship was obvious between these ratios for individual coal samples and their respective maturity (Table 2). These ratios are also summarized for vehicle emissions (auto and diesel) using petroleum products and for smoke from biomass burning in Table SI-1. The coal smoke PAH ratios do not differ significantly on comparison with the other source emission ratios. Therefore, if these ratios are used as distinguishing indicators for coal combustion, additional specific tracers would strengthen such a diagnostic of source apportionment.

Hydroxy-PAHs. Hydroxy-PAHs (arylphenols) were not found in extracts of the bulk coals. Simple and alkylated phenols have generally been reported for coal smoke and hydroxy-PAHs for some Chinese coal smoke emissions (*31*, *32*). Phenols were also identified in all of these coal smoke samples, however, they are excluded due to nonsource specificity and high volatility for effective sampling as aerosol PM. Monohydroxy-PAHs can be formed in vivo (*33*), by photochemical transformation in the atmosphere (*34*, *35*), and as reported here in coal smoke by direct emissions from a point source (Table 2).

The analytical aspects and examples of GC-MS results for hydroxy-PAHs are given in the Supporting Information section. The major hydroxy-PAHs found in coal smoke are naphthols, hydroxyfluorenes, phenanthrols, anthrols, hydroxypyrenes, hydroxyfluoranthenes, traces of higher molecular weight hydroxy-PAHs, and minor amounts of alkylhydroxy-PAHs (C_1 and C_2) (Table 2). These compounds were determined as the TMS derivatives.

The hydroxy-PAHs are not detectable in raw coal extracts (Bi, unpublished data). Thus, the close relationship between PAHs and hydroxy-PAHs indicates that the latter are formed by oxidation processes from PAHs. The ratios of individual PAHs (e.g., Phe+Ant) to the corresponding hydroxy-PAHs (e.g., OH-Phe+Ant, given as Phe/OH-Phe, Table 2) generally increase, and then decrease, with higher molecular weight ($MW > 202$). This implies that higher MW hydroxy-PAHs may form primarily in the vapor phase under the conditions of open fire and residential coal combustion. At present, the exact mechanism of hydroxy-PAH formation during combustion is not understood.

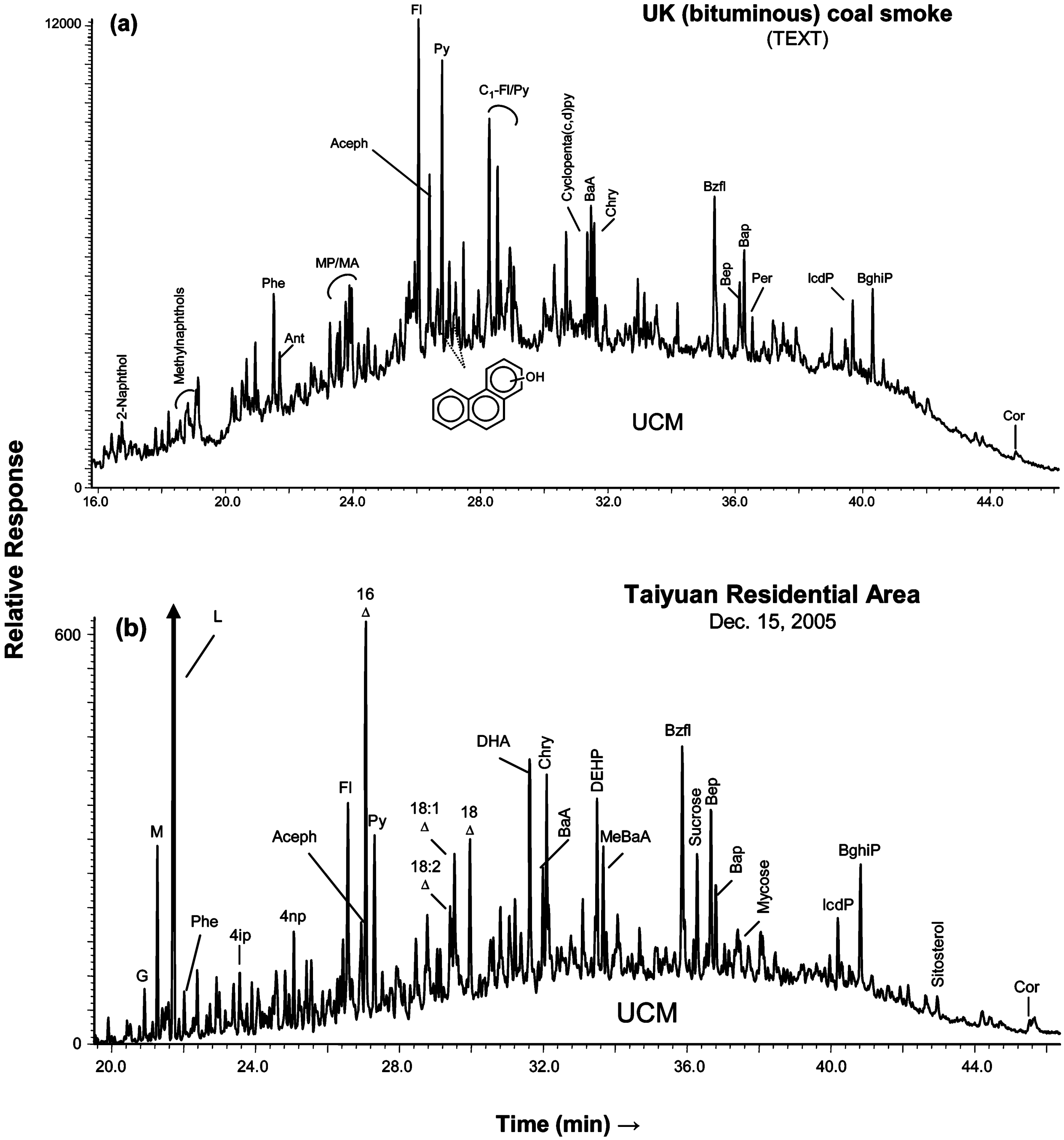

FIGURE 1. Annotated GC-MS total ion current traces for total extracts of (a) Smoke particles from open fire burning of UK bituminous coal (methylated with diazomethane), and (b) ambient aerosol TSP from Taiyuan, China in winter (silylated to TMS) (*L* = 2100, shown off scale). Symbols: UCM = unresolved complex mixture, *G* = galactosan, M = mannosan, *L* = levoglucosan, DHA = dehydroabietic acid, Phe = phenanthrene, Ant = anthracene, MP/MA = methylphenanthrenes/methylanthracenes, Fl = fluoranthene, Py = pyrene, Aceph = acephenanthrylene, BaA = benz[a]anthracene, Chry = chrysene, Bzfl = benzofluoranthenes, Bep = benzo[e]pyrene, Bap = benzo[a]pyrene, Per = perylene, IcdP = indeno[cd]pyrene, BghiP = benzo[ghi]perylene, Cor = coronene, 4i/np = dibutylphthalates, DEHP = diethylhexylphthalate, numbers over open triangles refer to fatty acids.

Source Ratio Parameters. PAHs and hydroxy-PAHs in coal smoke exhibit a different trend with maturity (rank). The ratios between PAHs and corresponding hydroxy-PAHs were calculated to assess whether these ratios can be used to identify the coal rank or type in smoke emissions. As defined above, the Phe/OH-Phe ratios were 2.7 for lignite, 1.03 for bituminous coal, and 0.12 for anthracite smoke (Table 2). The ratios of pyrene to hydroxypyrene (Py/OH-Py) and chrysene to hydroxychrysene (Chry/OH-Chry) are calculated as the total m/z 202 signal for fluoranthene plus pyrene plus acephenanthrylene divided by all isomers at m/z 290 (OH-Py/Fl), and the total m/z 228 signal for benzanthracene plus chrysene over all isomers at m/z 316 (OH-BaA/Chry), respectively (Table 2). The Py/OH-Py ratio was in the range of 7.2–19 for lignite, 1.4–34 for semi-bituminous and bituminous coal, generally higher than anthracite (2.0) smoke. The Chry/OH-Chry had a wide range of values for all coal smoke samples (lignite 8–17.5, anthracite 9.9, and bituminous coal 1.3–15.7). These ratios may be useful as indicators although they have wide ranges and do not show clear trends with coal rank. More source test data should refine these parameters. Nevertheless, the presence of the hydroxy-PAHs with these ratios may be used to apportion PAH and hydroxy-

TABLE 3. Smoke and Related Tracers in Some Ambient Urban Atmospheres (ng/m3) During Winter[a]

compound	Corvallis, OR	Guangzhou	Beijing	Taiyuan
alkanes				
n-hexadecane	nd	4.0	nd	11.2
n-heptadecane	nd	4.2	nd	28.7
n-octadecane	nd	7.5	15.2	37.1
n-nonadecane	nd	11.7	40.5	30.1
n-eicosane	nd	20.6	102.1	25.2
n-heneicosane	0.1	44.4	146.2	37.6
n-docosane	0.3	42.4	170.4	54.9
n-tricosane	0.7	52.1	180.9	60.4
n-tetracosane	1.0	57.3	148.4	63.4
n-pentacosane	1.1	62.7	128.1	58.2
n-hexacosane	0.7	40.0	80.6	40.0
n-heptacosane	0.6	41.5	60.1	33.3
n-octacosane	0.3	34.9	32.4	18.1
n-nonacosane	0.4	46.5	42.8	20.8
n-triacontane	nd	20.6	20.2	6.2
n-hentriacontane	0.1	49.1	24.9	10.9
n-dotriacontane	nd	13.4	8.8	nd
n-tritriacontane	nd	19.9	9.3	nd
n-tetratriacontane	nd	7.4	nd	nd
total	5.3	580.2	1210.9	536.1
CPI	0.80	1.46	1.06	1.10
Cmax	25	25	23	24
UCM	nd	2090	20563	10900
hopanes				
17α(H)-22,29,30-trisnorhopane	nd	1.4	12.1	9.1
17β(H)-22,29,30-trisnorhopane	nd	nd	8.2	nd
17α(H),21β(H)-29-norhopane	nd	6.2	22.2	16.2
17β(H),21α(H)-29-norhopane	nd	0.8	16.6	3.4
17α(H),21β(H)-hopane	nd	11.3	26.4	19.8
17β(H),21α(H)-hopane	nd	1.6	13.2	4.7
22S-17α(H),21β(H)-homohopane	nd	3.3	5.1	5.4
22R-17α(H),21β(H)-homohopane	nd	2.2	6.8	3.9
17β(H),21α(H)-homohopane	nd	nd	nd	nd
S-17α(H),21β(H)-bishomohopane	nd	1.9	3.1	2.9
R-17α(H),21β(H)-bishomohopane	nd	1.4	2.8	1.7
17β(H),21α(H)-bishomohopane	nd	0.3	nd	nd
total	nd	30.4	116.5	67.1
PAHs				
fluorene	nd	0.04	nd	nd
methylfluorenes	nd	nd	nd	nd
phenanthrene (Phe)	nd	1.8	16.1	35.4
anthracene (Ant)	nd	0.2	3.4	4.1
methylphenanthrenes	nd	1.8	42.0	111.4
3-methylphenanthrene	nd	0.4	7.0	27.0
2-methylphenanthrene	nd	0.4	10.0	32.0
9-methylanthracene	nd	0.1	4.0	6.0
9-methylphenanthrene	nd	0.5	8.0	25.0
1-methylphenanthrene	nd	0.4	13.0	21.0
fluoranthene (Fl)	0.002	5.0	84.8	160.1
acephenanthrylene	nd	0.9	21.2	70.8
pyrene (Py)	0.002	5.6	87.1	135.4
C_1−202	nd	nd	125.4	140.9
retene	0.004	2.0	25.3	13.5
benzo[ghi]fluoranthene	nd	5.6	36.3	58.5
cyclopenta[cd]pyrene	nd	6.8	24.0	20.4
benz[a]anthracene (BaA)	0.001	5.7	70.2	80.1
chrysene (Chry)	0.002	9.8	66.3	155.9
C_1−228	nd	nd	83.8	140.2
benzo[b+k]fluoranthenes	0.003	23.3	176.5	195.3
benzo[a]fluoranthene	nd	1.7	17.1	20.2
benzo[a]pyrene (BaP)	nd	7.7	45.6	63.7
benzo[e]pyrene (BeP)	0.001	11.1	50.4	120.2
perylene	nd	1.4	9.1	9.8
indeno[1,2,3,4-cdef]chrysene	nd	4.5	14.1	12.2
indeno[cd]pyrene (IcdP)	nd	11.1	30.1	52.6
benzo[ghi]perylene (BghiP)	nd	9.9	33.8	90.7
dibenz[ah]anthracene	nd	1.9	nd	nd

PAH sources in the atmosphere with the qualifiers mentioned above.

Coal Smoke Tracers in the Atmosphere. Samples of aerosol particles were analyzed as total extracts (TMS) from four areas in winter: Corvallis, OR (background, wood burning emissions, light traffic, no coal utilization), Guangzhou, P.R. China (semitropical mega-city, heavy traffic, no significant coal burning), Beijing and Taiyuan (temperate

TABLE 3. Continued.

compound	Corvallis, OR	Guangzhou	Beijing	Taiyuan
picene	nd	1.0	nd	12.2
triphenylbenzene	nd	2.4	11.9	4.2
total	**0.015**	**123.0**	**1116.5**	**1818.8**
Phe/(Phe+Ant)	nd	0.90	0.83	0.90
Fl/(Fl+Py)	0.50	0.47	0.49	0.54
BaA/(BaA+Chry)	0.33	0.37	0.51	0.34
BeP/(BeP+BaP)	nd	0.59	0.53	0.65
IcdP/(IcdP+BghiP)	nd	0.53	0.47	0.37
hydroxy-PAHs				
naphthols	nd	nd	nd	4.1
methylnaphthols	nd	nd	nd	19.2
dimethylnaphthols	nd	nd	nd	17.7
hydroxyfluorenes	nd	nd	39.7	72.3
C_1−182	nd	nd	61.9	88.5
C_2−182	nd	nd	22.7	18.7
phenanthrols+anthrols	nd	nd	32.9	68.7
C_1−194	nd	nd	24.9	72.9
hydroxypyrenes+fluoranthenes	nd	1.8	29.2	26.4
C_1−218	nd	nd	11.7	22.6
hydroxychrysenes (OH-Chry)+benzanthrols	nd	nd	10.5	6.3
hydroxybenzo[a/e]pyrenes (OH−BaP)	nd	nd	8.1	nd
total	nd	**1.8**	**241.6**	**417.4**
Phe/OH-Phe	nd	nd	0.59	0.57
Py/OH-Py	nd	6.40	6.61	13.90
Chry/OH-Chry	nd	nd	13.00	37.50
BaP/OH−BaP	nd	nd	38.80	nd
PAHs/OH-PAHs	nd	66.00	4.30	4.10
"biomass smoke"	nd	nd	nd	nd
dehydroabietic acid	33.3	30.1	212.9	170.0
levoglucosan	1503.8	629.4	10524.0	919.0

[a] nd, not detected.

mega-cities, major coal burning and traffic). The relevant ambient concentrations of the coal smoke and related tracers are given in Table 3. Data has also been reported for Nanjing, China (*36*).

An example of the salient features of the GC-MS data for a total extract (silylated) of urban aerosol particles is shown in Figure 1b and in the Supporting Information as Figure SI-3. The major resolved compounds are levoglucosan, with mannosan and galactosan, and dehydroabietic acid from biomass burning; fatty acids, sterols, and phthalates from numerous sources, and PAHs (Table 3). The UCM represents the largest mass fraction. The hydroxy-PAHs are minor peaks and are best identified by key ion search of the GC-MS data for their molecular ions as illustrated in the Supporting Information section. The significant concentrations of hydroxy-PAHs in the northern China aerosols confirm coal smoke emissions, especially when combined with the distribution patterns of the isomers (molecular ions) which are similar for hydroxy-PAHs in coal smoke and ambient aerosol PM (for example, compare Figures SI-2c,d vs SI-3d,e and SI-2g vs SI-3g).

The hydroxy-PAHs are detectable in the atmospheres of Beijing and Taiyuan (242 ng/m^3 and 417 ng/m^3, respectively, Table 3) and Nanjing, central eastern China (180−420 ng/m^3, *36*), but not in Corvallis or Guangzhou. The ratios of total PAHs to total hydroxy-PAHs is about 4.0 for both northern Chinese cities, similar to bituminous coal smoke, whereas for Nanjing it is about 0.5 (*36*). Thus, organic compounds from coal smoke are part of the total atmospheric loading and the other compound groups can be apportioned to emissions from petroleum product use (i.e., traffic), biomass burning and coal burning. The emissions from biomass burning comprise mainly levoglucosan, lignin derived phenols, retene, and dehydroabietic acid (Table 3, *6*).

The emissions source apportionment of coal smoke versus traffic (both diesel and gasoline engines) is an important aspect for urban areas where these fossil fuels are used. A previous report applied the maturity ratio of the homohopane tracers as indicator for coal smoke (*13*). This ratio and the relatively higher levels of moretanes, compared to hopanes, can be used as indicators for coal smoke, but for coals of low

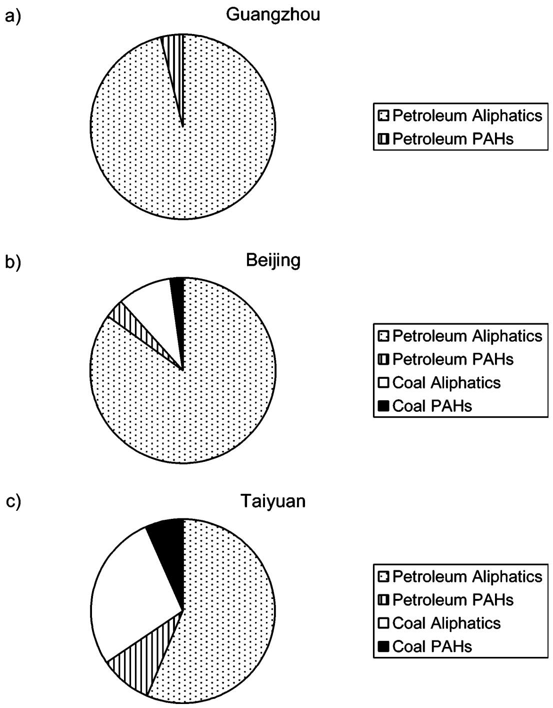

FIGURE 2. Pie diagrams showing the apportionment of the urban hydrocarbons to fossil fuel sources, i.e., petroleum product use and coal burning (the aliphatic hydrocarbons are the apportioned alkanes and UCM): (a) Guangzhou, (b) Beijing, and (c) Taiyuan.

rank (not bituminous to anthracite) (*12*). However, burning of peat and tropical biomass can also introduce those same tracers into smoke (*26*).

Therefore, utilizing the specific tracers for coal smoke, as such or in conjunction with hopane parameters, is more definitive for source discrimination of fossil fuel emissions to the ambient atmosphere. Here we assign all hydroxy-PAHs to coal smoke and apportion the PAHs, UCM and alkanes according to the source emissions from the coal stove tests (Table SI-2). It should be noted that biomass burning does not emit hydroxy-PAHs. The results are shown graphically in the pie diagrams (Figure 2), where Guangzhou has no coal smoke signal and both northern Chinese cities are heavily impacted by coal burning.

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Supporting Information Available

Background information about coal combustion chemistry, examples of GC-MS data for total extracts of coal smoke PM samples and an ambient aerosol PM sample with related discussion of the results, a comparison table of PAH ratios for source emission tests from the literature, and an apportionment table for coal versus petroleum components. This material is available free of charge via the Internet at http://pubs.acs.org.

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