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Supplementary Information

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Effect of Dibenzopyrene Measurement on Assessing Air Quality in Beijing Air and Possible Implications for Human Health

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Table S1. PAH analyte list. Class 1, 2A and 2B (carcinogenic, possible and probable human carcinogens) are listed as carcinogenic according to the International Agency for Research on Cancer. [1]

PAH	Ring #	Designation	Abbreviation	Formula
Naphthalene	2	Other Non-Substituted	NAP	$C_{10}H_8$
2-Methylnaphthalene	2	Alkylated PAH	1-mNAP	$C_{11}H_{10}$
1-Methylnaphthalene	2	Alkylated PAH	2-mNAP	$C_{11}H_{10}$
Naphthalene, 1,6-dimethyl-	2	Alkylated PAH	1,6-dmNAP	$C_{12}H_{12}$
Acenaphthylene	3	Other Non-Substituted	ACY	$C_{12}H_8$
Naphthalene, 1,2-dimethyl-	2	Alkylated PAH	1,2-dmNAP	$C_{12}H_{12}$
Acenaphthene	3	Other Non-Substituted	ACE	$C_{12}H_{10}$
Fluorene	3	Other Non-Substituted	FLU	$C_{13}H_{10}$
Dibenzothiophene	3	Sulfur-PAH	DBT	$C_{12}H_8S$
Phenanthrene	3	Other Non-Substituted	PHE	$C_{14}H_{10}$
Anthracene	3	Other Non-Substituted	ANT	$C_{14}H_{10}$
Fluoranthene	4	Other Non-Substituted	FLA	$C_{16}H_{10}$
Pyrene	4	Other Non-Substituted	PYR	$C_{16}H_{10}$
Retene	3	Alkylated PAH	RET	$C_{18}H_{18}$
1-Methylpyrene	4	Alkylated PAH	1-mPYR	$C_{17}H_{12}$
Benz[*a*]anthracene	4	Carcinogenic	BaA	$C_{18}H_{12}$
Chrysene	4	Carcinogenic	CHR	$C_{18}H_{12}$
Chrysene, 6-methyl-	4	Alkylated PAH	6-mCHR	$C_{19}H_{14}$
Benzo[*b*]fluoranthene	5	Carcinogenic	BbF	$C_{20}H_{12}$
Benzo[*k*]fluoranthene	5	Carcinogenic	BkF	$C_{20}H_{12}$
Benzo[*a*]pyrene	5	Carcinogenic	BaP	$C_{20}H_{12}$
Indeno[*1,2,3-c,d*]pyrene	6	Carcinogenic	I[cd]P	$C_{22}H_{12}$
Dibenz[*a,h*]anthracene	5	Carcinogenic	D[ah]A	$C_{22}H_{14}$
Benzo[*ghi*]perylene	6	Other Non-Substituted	B[ghi]P	$C_{22}H_{12}$
Dibenzo[*a,l*]pyrene	6	Carcinogenic	D[a,l]P	$C_{24}H_{14}$
Dibenzo[*a,e*]pyrene	6	Carcinogenic	D[a,e]P	$C_{24}H_{14}$
Dibenzo[*a,h*]pyrene	6	Carcinogenic	D[a,h]P	$C_{24}H_{14}$
Dibenzo[*a,i*]pyrene	6	Carcinogenic	D[a,i]P	$C_{24}H_{14}$
Dibenzo[*a,e*]fluoranthene*	6	Other Non-Substituted	D[a,e]F	$C_{24}H_{14}$
Dibenzo[*j,l*]fuoranthene*	6	Other Non-Substituted	D[j,l]F	$C_{24}H_{14}$
Dibenzo[*b,k*]fuoranthene*	6	Other Non-Substituted	D[b,k]F	$C_{24}H_{14}$
Naphtho[*2,3-b*]fluoranthene*	6	Other Non-Substituted	N[2,3-b]F	$C_{24}H_{14}$

*Limited carcinogenicity information

Table S2. PAHs recovered from National Institute of Standards and Technology (NIST) Standard Reference Materials (SRMs).[2]

Analyte Recovery of NIST SRM 1649b: Urban Dust

n = 6 Analyte	Certified Value (mg kg^{-1})	AVG Measured (mg kg^{-1})	AVG Recovery (%)	RSD (%)
Phenanthrene	3.941	3.55	90.0	6
Fluoranthene	6.14	5.94	96.7	5
Pyrene	4.784	4.73	98.9	5
Benz[a]anthracene	2.092	1.95	93.3	10
Chrysene	3.008	2.76	91.8	7
Benzo[b]fluoranthene	5.99	6.54	109.2	6
Benzo[k]fluoranthene	1.748	1.85	105.7	11
Benzo[a]pyrene	2.47	2.10	85.1	7
Indeno[1,2,3-c,d]pyrene	2.96	2.56	86.5	3
Dibenz[a,h]anthracene	0.29	0.54	123.9	8
Benzo[ghi]perylene	3.937	3.96	100.5	6
Dibenzo[a,e]pyrene	0.538	0.58	109.5	6
Dibenzo[b,k]fluoranthene	0.655	0.69	104.7	5

Analyte Recovery of NIST SRM 1491a: Methyl-Substituted Polycyclic Aromatic Hydrocarbons

n = 3 Analyte	Certified Value (μg mL^{-1})	AVG Measured (μg mL^{-1})	AVG Recovery (%)	RSD (%)
2-Methylnaphthalene	1.76	1.69	96.3	5
1-Methylnaphthalene	1.52	1.39	91.2	3
Naphthalene, 1,6-dimethyl-	1.39	1.26	90.3	2
Naphthalene, 1,2-dimethyl-	1.72	1.63	94.5	1
Retene	1.80	1.85	102.8	0
1-Methylpyrene	0.94	0.98	104.3	3
Chrysene, 6-methyl-	1.04	1.01	97.2	3

AVG = average, RSD = relative standard deviation

Table S3. Recoveries of dibenzopyrene isomers from Standard Reference Material 1649b.

Mean Recoveries of Molecular Weight 302 isomers from Urban Dust SRM 1649b

		mg kg^{-1} with St Dev		
		This study	Bergvall et al 2008[3]	NIST[2]
Number	PAH	$n = 6$	$n = 4$[a]	Certified Value
1	Dibenzo[*a,l*]pyrene	0.028 (0.004)	0.019 (0.002)	0.054 (0.002)[b]
2	Dibenzo[*a,e*]pyrene	0.589 (0.037)	0.456 (0.036)	0.538 (0.025)
3	Dibenzo[*a,h*]pyrene	0.0442 (0.004)	0.06 (0.007)	na
4	Dibenzo[*a,i*]pyrene	0.133 (0.018)	0.149 (0.014)	na
5	Dibenzo[*j,l*]fluoranthene	0.464 (0.066)	na	0.356 (0.018)[b]
6	Dibenzo[*b,k*]fluoranthenec	0.686 (0.034)	na	0.655 (0.035)
7	Naphtho[*2,3-b*]fluoranthene	0.153 (0.011)	na	0.147 (0.011)[b]

na= not reported, [a]analyzed SRM1649a, [b]Reference Value, [c]Dibenzo[*b,k*]fluoranthene could not be separated from Dibenzo[*a,e*]fluoranthene in this study and it was not reported from Bergavall et al or NIST
This study and Bergvall et al utlized a 60 m DB-17MS column with 0.15μm film thickness, and
NIST used a 60 m DB-17MS with 0.25 μm film thickness and a proprietary column

Table S4. Summer (n = 7) and winter (n = 8) measured PAH concentrations (pg m^{-3}) on three size fractions of airborne particulate matter: $PM_{7.2}$, $PM_{1.5\text{-}7.2}$ and $PM_{1.5}$. PAHs are organized by classification and normalized per cubic meter of air sampled.

	24 h Mean Concentrations (St Dev)											
Season:	Summer						Winter					
PAH (pg m^{-3} air)	$PM_{7.2}$		$PM_{1.5\text{-}7.2}$		$PM_{1.5}$		$PM_{7.2}$		$PM_{1.5\text{-}7.2}$		$PM_{1.5}$	
Carcinogenic*												
BaA	25.4	(5)	53.4	(17)	634	(115)	333	(151)	2080	(1080)	17400	(9530)
CHR	48.2	(11)	154	(66)	945	(190)	346	(170)	1960	(1170)	24500	(9800)
BbF	n/a		n/a		3530	(1650)	308	(154)	2030	(1130)	35000	(13100)
BkF	n/a		n/a		974	(357)	87.5	(43)	534	(278)	13200	(6170)
BaP	nd		nd		714	(75)	140	(70)	943	(509)	23500	(11200)
I[cd]P	39.3	(6)	192	(51)	1920	(157)	164	(72)	836	(342)	8320	(2670)
D[ah]A	nd		nd		354	(69)	nd		278	(100)	3790	(1160)
D[a,l]P	nd		nd		23	(14)	nd		14	(4)	2869	(1200)
D[a,e]P	7.8	(1)	15	(7)	259	(39)	24	(10)	152	(73)	29300	(11800)
D[a,h]P	nd		nd		15	(2)	8	(2)	36	(18)	6190	(2530)
D[a,i]P	nd		nd		53	(18)	12	(4)	55	(23)	9930	(4450)
Alkylated												
2-mNAP	nd		nd		44.6	(5)	37.2	(24)	50.6	(19)	344	(89)
1-mNAP	nd		nd		nd		24.7	(14)	39.5	(13)	325	(101)
1,6-dmNAP	nd		nd		nd		22.9	(6)	45.4	(14)	391	(84)
1,2-dmNAP	nd		nd		nd		nd		nd		nd	
1-mPYR	nd		nd		87.2	(20)	151	(22)	537	(245)	6150	(2310)
6-mCHR	nd		nd		nd		47.7	(15)	261	(85)	2560	(1000)
RET	23.0	(8)	39.1	(7)	124	(26)	645	(281)	2910	(1380)	30000	(14900)
Sulfur												
DBT	nd		nd		nd		121	(36)	364	(183)	3590	(1460)
Non-Substituted												
ACY	nd		nd		25.4	(4)	65.7	(23)	151	(63)	2140	(783)
NAP	8.6	(3)	13.0	(3)	37.1	(11)	70.9	(39)	88.9	(35)	288	(67)
ACE	nd		nd		nd		nd		nd		nd	
FLU	nd		nd		50.5	(8)	96.8	(54)	276	(137)	3300	(1190)
PHE	35.3	(6)	85.7	(26)	430	(56)	786	(379)	3090	(1620)	37000	(15800)
ANT	nd		8.7	(1)	65.5	(20)	227	(133)	787	(449)	8030	(3190)
FLA	31.1	(11)	118	(83)	606	(118)	856	(441)	4100	(2560)	38900	(16500)
PYR	41.6	(4)	135	(49)	824	(116)	766	(346)	4100	(2170)	75400	(35300)
B[ghi]P	34.9	(5)	152	(37)	2160	(195)	143	(63)	879	(432)	22500	(10400)
D[j,l]F	7.6	(1)	22	(6)	280	(29)	21	(9)	129	(65)	25050	(14100)
ΣD[b,k+a,e]F	9.8	(1)	31	(11)	397	(45)	29	(13)	187	(92)	45600	(18600)
N[2,3-b]F	nd		nd		120	(21)	11	(7)	89	(46)	17950	(10200)
Σ PAHs pg m^{-3}	292	(76)	881	(493)	14600	(2870)	5340	(2450)	26700	(14000)	493000	(206000)

*IARC Classified Carcinogens[1], Bold represents the EPA 16 Priority Pollutant PAHs

n/a= data not available due to interferring compound for quantification, nd = not detected, St Dev = standard deviation

Table S5. PAH diagnostic ratios from $PM_{1.5}$ with mean and standard deviation (in parentheses)

Ratio	BaA/ CHR	PYR/ BaP	B[ghi]P/ BaP	FLA/ (FLA+ PYR)	IPY/ (IPY+ B[ghi]P)	IcdP/ B[ghi]P	BbF/ BkF	B[ghi]P/ I[cd]P	1mPYR/ PYR	$PM_{1.5}$/ PM_{10}
Summer	0.7 (0.2)	1.2 (0.1)	3.1 (0.4)	0.4 (0.1)	0.5 (0.0)	0.9 (0.0)	3.8 (0.4)	1.1 (0.1)	0.1 (0.0)	0.7 (0.0)
Winter	0.7 (0.2)	3.2 (0.2)	1.0 (0.1)	0.4 (0.0)	0.3 (0.1)	0.5 (0.1)	3.0 (0.5)	2.4 (0.5)	0.1 (0.0)	0.9 (0.0)

PM10 = Σ $PM_{1.5}$ and $PM_{1.5\text{-}7.2}$

Taken alone, the use of PAH ratios to distinguish sources may be questionable since Beijing air is a myriad of emission sources, but they do provide a useful tool for comparison. An IPY/(IPY+BghiP) ratio of 0.47 ± 0.01 (summer) and 0.31 ± 0.1 (winter) was observed from this study. Zhou et al measured similar ratios, suggesting the lower wintertime ratio resulted from increased coal use in Beijing winters.[4] Diagnostic ratios are widely reported for PAHs and Zhang et al concluded air to be the most stable sample media for PAH preservation of source ratios compared to other media.[5] However, caution should be used when assigning sources based on diagnostic ratios alone. For example, PYR/BaP ratios of 1.2 in the summer and 3.2 in the winter may be interpreted as indicative of different sources. On the other hand, the seasonal difference could have resulted from a suite of other factors including increased emissions of PYR in the winter, increased temperature-facilitated partitioning to the particulate phase during the cold season, or ratio shifts could also be a product of greater photodecomposition of PYR during the summer. Furthermore, a few ratios were consistent between seasons: BaA/CHR of 0.7, FLA/(FLA+PYR) of 0.4 and 1mPYR/PYR of 0.1. Traditionally, IPY/(IPY+BghiP) ratios of 0.18, 0.37, and 0.56 have been used to characterize gasoline, diesel, and coal/coke emissions respectively;[6] a recent study characterizing the emissions from Chinese coals by industrial and residential combustion, reported values of 0.50, 0.57 and 0.35 for industrial, residential, and coal briquette combustion respectively.[7]

PM Mass ratios (PM2.5/PM10) have been shown to reflect different sources. Typically higher ratios (>0.5) are indicative of anthropogenic over natural sources.[8] In this study PM1.5/PM10 were 0.7 and 0.9 during the summer and winter respectively. The enrichment of smaller particles in the winter could indicate different or increased anthropogenic combustion sources. The mass ratio six years prior was reported much lower at 0.45-0.48 and 0.5-0.7 in summer and winter respectively.[9]

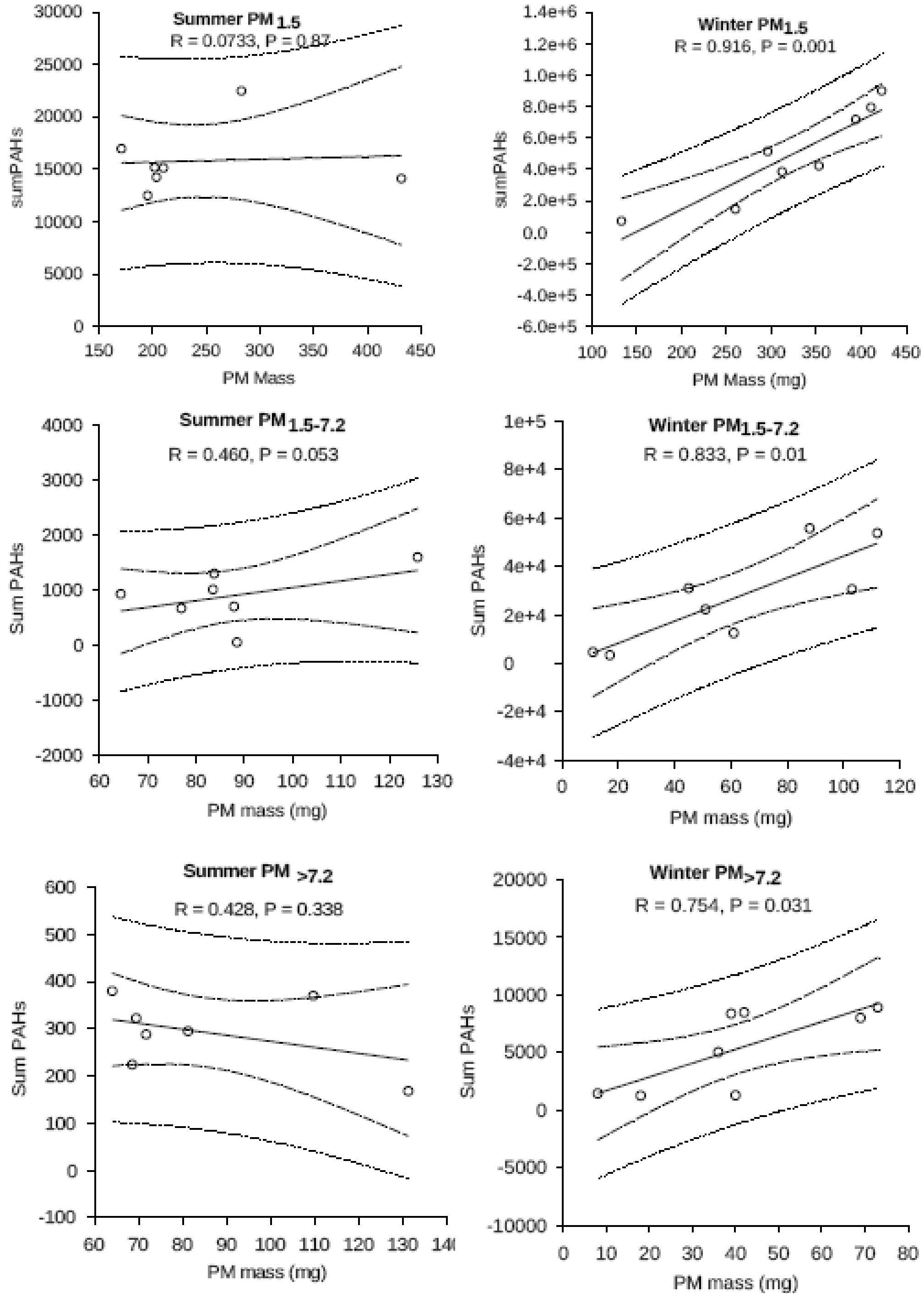
Table S6. Seasonal PM Mass and T tests showing no significant difference ($p > 0.05$) between summer ($n = 7$) and winter ($n = 8$) PM mass for $PM_{1.5}$ and PM_{10}, but reflects a significant difference for $PM_{1.5\text{-}7.2}$ and $PM_{7.2}$.

24 h Particulate Matter Mass Concentrations µg m^{-3}

PM Mass	$PM_{1.5}$			$PM_{1.5\text{-}7.2}$			$PM_{7.2*}$		PM_{10}		
Season:	Mean	*t*	*p*	Mean	*t*	*p*	Median	*p*	Mean	*t*	*p*
Summer	163.4	0.75	0.47	57.7	2.17	0.05	46.4	0.004	221.1	0.12	0.91
Winter	190.2			36.3			23.5		226.4		

P-values *(p)* were obtained from Student's T test or *Mann-Whitney Rank Sum if normality failed, $PM_{10} = \Sigma PM_{1.5} + PM_{1.5\text{-}7.2}$

Figure S1. Correlations of PAHs to PM according to PM size fraction



Linear regressions of the sum of PAHs (pg m^{-3}) to PM mass per size fraction of PM ($PM_{1.5}$ (top), $PM_{1.5\text{-}7.2}$ (middle) and $PM_{7.2}$ (bottom)) during both seasons. The solid line represents the regression line, while the inner and outer dash sets display the confidence and prediction intervals respectively. Correlations are considered significant if $p < 0.05$.

Table S7. Mean meteorological parameters (standard deviation) obtained by NOAA ARL with GDAS1 archived data (http://www.ready.noaa.gov/ready/amet.html).

Mean Meterological Conditions

Parameter	Pressure		Temp		Dew point		Thickness		Height		Wind Speed		Humidity		Precipitation	
Units	hpa		°C		n/a		n/a		dm		knots		%		mm	
Winter	1036.1	(5)	-7.5	(2)	-20.4	(4)	519.2	(5)	547.4	(3)	3.9	(1)	39.3	(14)	0.0	(0)
Summer	1008.9	(3)	25.9	(2)	13.7	(2)	578.4	(2)	586.2	(4)	3.1	(1)	52.1	(8)	0.0	(0)

hpa = hectopascal, dm = decimeter, mm = millimeters

Data was retrieved for Beijing, China (lat 39.9, long 116.4). Data was collected by NOAA every 3 hours at 500 millibar, unless otherwise specified, and averaged for each 24 hour sample period. It is noteworthy that a recent PM study from Beijing applied a humidity correction to PM mass measurement. Wang et al 2009 observed a large spread of relative humidity (40-90%),[10] but humidity effects for this study are expected to be negligible since lower relative humidity was recorded and standard protocols for mass measurements were followed. For example, humidity was highest during summer, ranging from 42-65%. Corrections from Wang et al 2009 would result in 1 +/-3 μg m^{-3} change in PM mass.[10]

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