Supplementary Information

Manuscript Title:

Effect of Dibenzopyrene Measurement on Assessing Air Quality and Cancer Risk in Beijing Air

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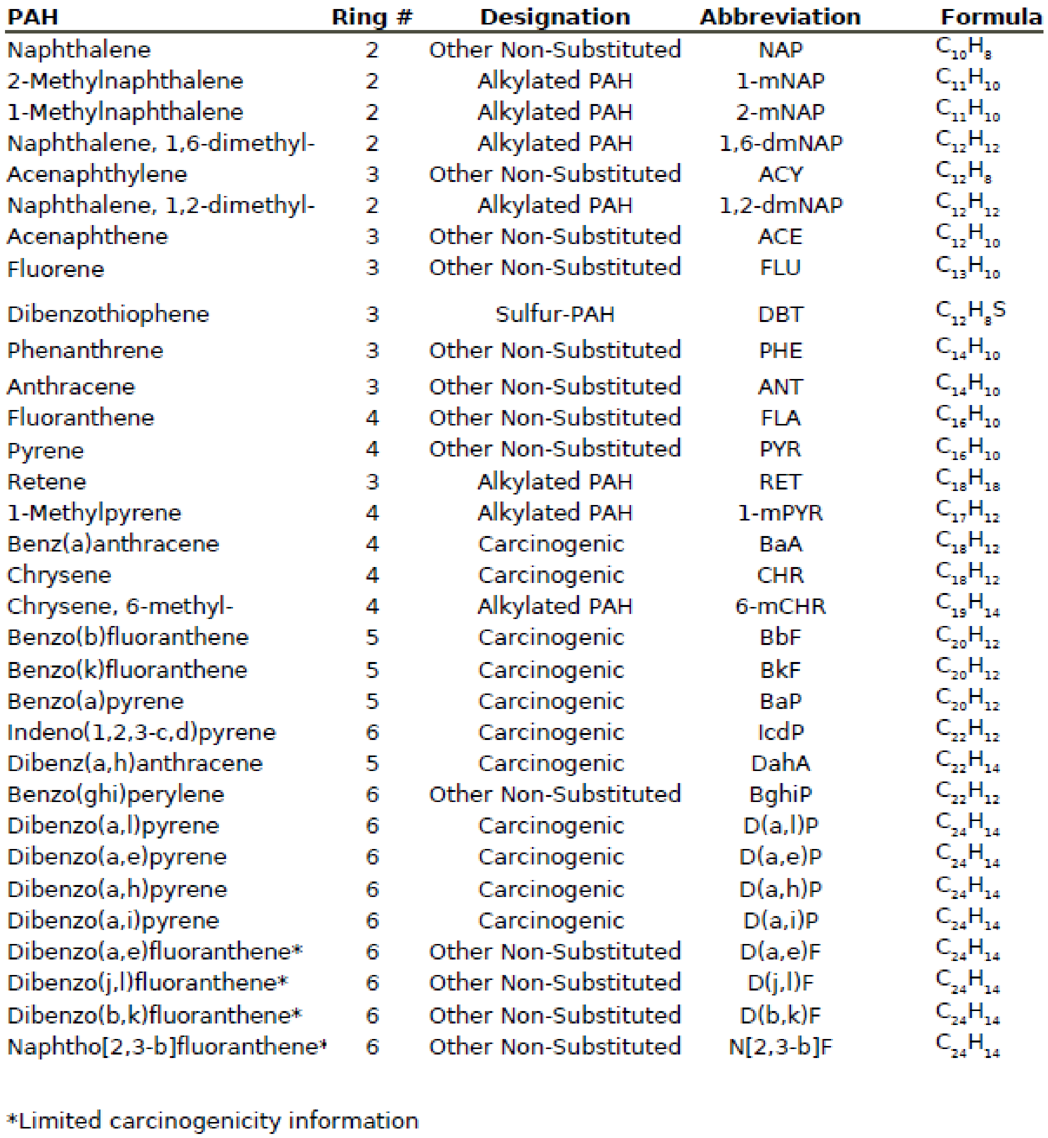
Table 1 PAH analyte list monitored by GC-MS with number of fused benzene rings, grouping designation, abbreviation and chemical formula. Carcinogenic PAHs included those determined as IARC class 1, 2A and 2B (carcinogenic, possible and probable human carcinogens)[1].



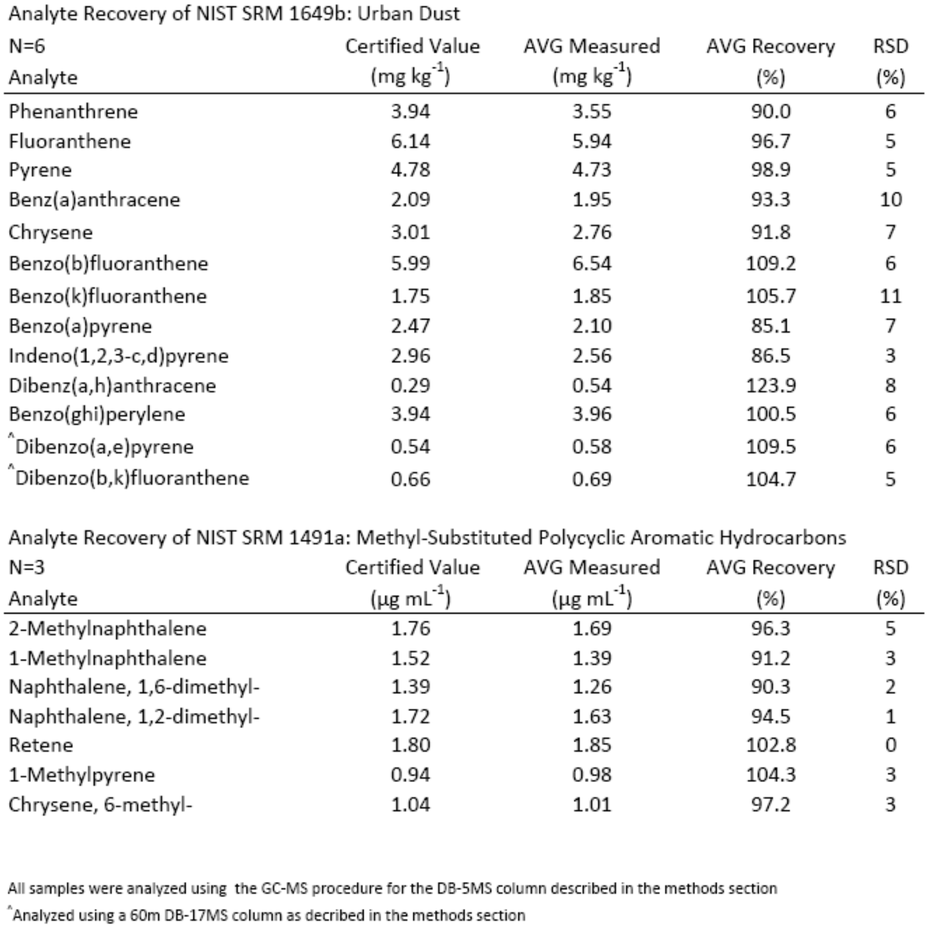
PAH	Ring #	Designation	Abbreviation	Formula
Naphthalene	2	Other Non-Substituted	NAP	$C_{10}H_{8}$
2-Methylnaphthalene	2	Alkylated PAH	1-mNAP	$C_{11}H_{10}$
1-Methylnaphthalene	2	Alkylated PAH	2-mNAP	$C_{11}H_{10}$
Naphthalene, 1,6-dimethyl-	2	Alkylated PAH	1,6-dmNAP	$C_{12}H_{12}$
Acenaphthylene	3	Other 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	$C_{12}H_{8}S$
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	IcdP	$C_{22}H_{12}$
Dibenz(a,h)anthracene	5	Carcinogenic	DahA	$C_{22}H_{14}$
Benzo(ghi)perylene	6	Other Non-Substituted	BghiP	$C_{22}H_{12}$
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)fluoranthene*	6	Other Non-Substituted	D(j,l)F	$C_{24}H_{14}$
Dibenzo(b,k)fluoranthene*	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

References:

[1] IARC (1983,2008). Polynuclear Aromatic Compounds, Part 1 & Air Pollution, Part 1. Lyon, France. **32 and 92**.

Table 2 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	3.94	3.55	90.0	6
Fluoranthene	6.14	5.94	96.7	5
Pyrene	4.78	4.73	98.9	5
Benz(a)anthracene	2.09	1.95	93.3	10
Chrysene	3.01	2.76	91.8	7
Benzo(b)fluoranthene	5.99	6.54	109.2	6
Benzo(k)fluoranthene	1.75	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	3.94	3.96	100.5	6
^Dibenzo(a,e)pyrene	0.54	0.58	109.5	6
^Dibenzo(b,k)fluoranthene	0.66	0.69	104.7	5

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

N=3 Analyte	Certified Value ($\mu g\ mL^{-1}$)	AVG Measured ($\mu g\ mL^{-1}$)	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

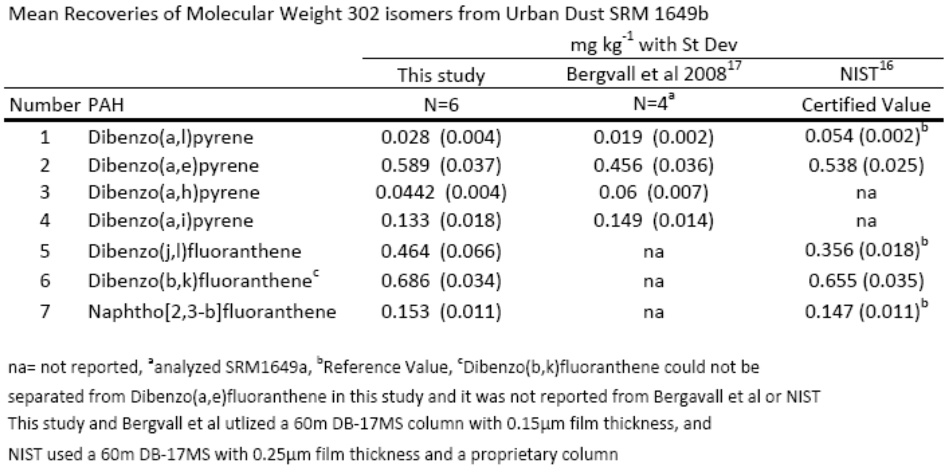
All samples were analyzed using the GC-MS procedure for the DB-5MS column described in the methods section

^Analyzed using a 60m DB-17MS column as decribed in the methods section

References:

[2] NIST, National Institute of Standards and Technology, Gaithersburg, MD, Certification of Analysis, 2009.

Table 3.



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

		mg kg^{-1} with St Dev		
		This study	Bergvall et al 2008[17]	NIST[16]
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)fluoranthene[c]	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 60m DB-17MS column with 0.15µm film thickness, and NIST used a 60m DB-17MS with 0.25µm film thickness and a proprietary column

Table 4

	24 h Mean Concentrations (St Dev)											
Season:	Summer						Winter					
PAH (pg m^{-3} air)	PM$_{7.2}$		PM$_{1.5-7.2}$		PM$_{1.5}$		PM$_{7.2}$		PM$_{1.5-7.2}$		PM$_{1.5}$	
Carcinogenic*												
Benz(a)anthracene	25.4	(5)	53.4	(17)	634	(115)	333	(151)	2080	(1080)	17400	(9530)
Chrysene	48.2	(11)	154	(66)	945	(190)	346	(170)	1960	(1170)	24500	(9800)
Benzo(b)fluoranthene	n/a		n/a		3530	(1650)	308	(154)	2030	(1130)	35000	(13100)
Benzo(k)fluoranthene	n/a		n/a		974	(357)	87.5	(43)	534	(278)	13200	(6170)
Benzo(a)pyrene	nd		nd		714	(75)	140	(70)	943	(509)	23500	(11200)
Indeno(1,2,3-c,d)pyrene	39.3	(6)	192	(51)	1920	(157)	164	(72)	836	(342)	8320	(2670)
Dibenz(a,h)anthracene	nd		nd		354	(69)	nd		278	(100)	3790	(1160)
Dibenzo(a,l)pyrene	nd		nd		23	(14)	nd		14	(4)	2869	(1200)
Dibenzo(a,e)pyrene	7.8	(1)	15	(7)	259	(39)	24	(10)	152	(73)	29300	(11800)
Dibenzo(a,h)pyrene	nd		nd		15	(2)	8	(2)	36	(18)	6190	(2530)
Dibenzo(a,i)pyrene	nd		nd		53	(18)	12	(4)	55	(23)	9930	(4450)
Alkylated												
2-Methylnaphthalene	nd		nd		44.6	(5)	37.2	(24)	50.6	(19)	344	(89)
1-Methylnaphthalene	nd		nd		nd		24.7	(14)	39.5	(13)	325	(101)
Naphthalene, 1,6-dimethyl-	nd		nd		nd		22.9	(6)	45.4	(14)	391	(84)
Naphthalene, 1,2-dimethyl-	nd		nd		nd		nd		nd		nd	
1-Methylpyrene	nd		nd		87.2	(20)	151	(22)	537	(245)	6150	(2310)
Chrysene, 6-methyl-	nd		nd		nd		47.7	(15)	261	(85)	2560	(1000)
Retene	23.0	(8)	39.1	(7)	124	(26)	645	(281)	2910	(1380)	30000	(14900)
Sulfur												
Dibenzothiophene	nd		nd		nd		121	(36)	364	(183)	3590	(1460)
Non-Substituted												
Acenaphthylene	nd		nd		25.4	(4)	65.7	(23)	151	(63)	2140	(783)
Naphthalene	8.6	(3)	13.0	(3)	37.1	(11)	70.9	(39)	88.9	(35)	288	(67)
Acenaphthene	nd		nd		nd		nd		nd		nd	
Fluorene	nd		nd		50.5	(8)	96.8	(54)	276	(137)	3300	(1190)
Phenanthrene	35.3	(6)	85.7	(26)	430	(56)	786	(379)	3090	(1620)	37000	(15800)
Anthracene	nd		8.7	(1)	65.5	(20)	227	(133)	787	(449)	8030	(3190)
Fluoranthene	31.1	(11)	118	(83)	606	(118)	856	(441)	4100	(2560)	38900	(16500)
Pyrene	41.6	(4)	135	(49)	824	(116)	766	(346)	4100	(2170)	75400	(35300)
Benzo(ghi)perylene	34.9	(5)	152	(37)	2160	(195)	143	(63)	879	(432)	22500	(10400)
Dibenzo(j,l)fluoranthene	7.6	(1)	22	(6)	280	(29)	21	(9)	129	(65)	25050	(14100)
ΣDibenzo(b,k+a,e)fluoranthene	9.8	(1)	31	(11)	397	(45)	29	(13)	187	(92)	45600	(18600)
Naphtho[2,3-b]fluoranthene	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, IARC (1983,2008)[14]

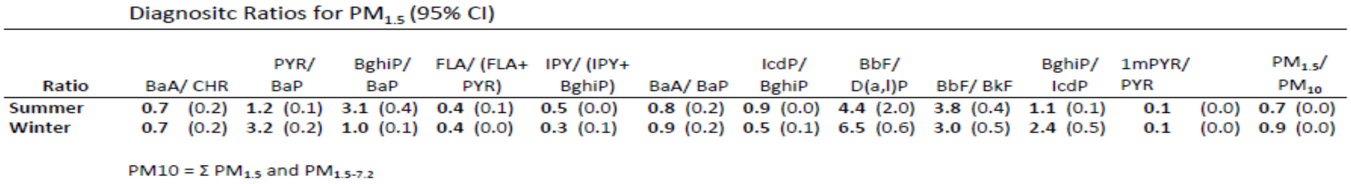
Bold represents the EPA 16 Priority Pollutant PAHs

nd = not detected

n/a= data not available due to interferring compound for quantification

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$_{1.5-7.2}$ and PM$_{1.5}$. PAHs are organized by classification and normalized per cubic meter of air sampled.

Table 5 PAH diagnostic ratios obtained from $PM_{1.5}$ with mean and 95% CI (in parentheses)



Diagnositc Ratios for $PM_{1.5}$ (95% CI)

Ratio	BaA/ CHR	PYR/ BaP	BghiP/ BaP	FLA/ (FLA+ PYR)	IPY/ (IPY+ BghiP)	BaA/ BaP	IcdP/ BghiP	BbF/ D(a,l)P	BbF/ BkF	BghiP/ IcdP	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)	**0.8** (0.2)	**0.9** (0.0)	**4.4** (2.0)	**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)	**0.9** (0.2)	**0.5** (0.1)	**6.5** (0.6)	**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) is observed from this study. Zhou et al measured similar ratios, suggesting the lower wintertime ratio resulted from increased coal use in Beijing winters[3]. Diagnostic ratios are widely reported in air. Zhang et al concluded air to be the most stable sample media for PAH preservation of source ratios compared to other media[4], 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 can be interpreted as indicative of different sources. On the other hand, the seasonal difference could result 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[5]; a recent study characterizing the emissions from Chinese coals by industrial and residential combustion, report values of 0.50, 0.57 and 0.35 for industrial, residential, and coal briquette combustion respectively[6].

PM Mass ratios ($PM_{2.5}/PM_{10}$) have been shown to reflect different sources. Typically higher ratios (>0.5) are indicative of anthropogenic over natural sources[7]. In this study $PM_{1.5}/PM_{10}$ 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 [8].

References

3. J. Zhou, Wang, T., Huang, Y., Mao, T., Zhong, N., Size distribution of polycyclic aromatic hydrocarbons in urban and suburban sites of Beijing, China *Chemoshere*, 2005, **61**, 792-799.
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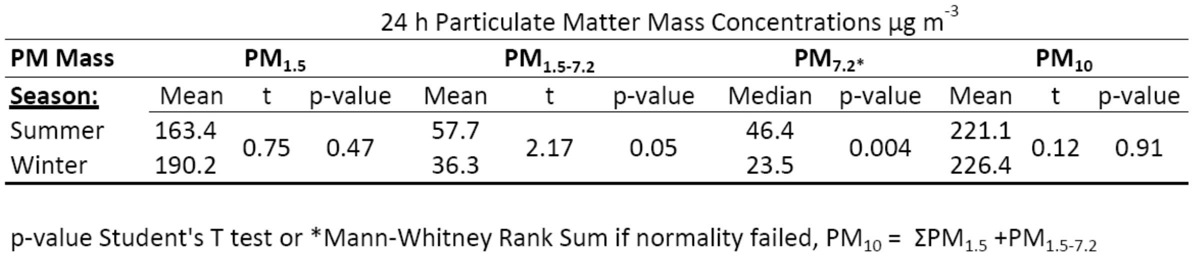
5. Duan, J. C.; Bi, X. H.; Tan, J. H.; Sheng, G. Y.; Fu, J. M., Seasonal variation on size distribution and concentration of PAHs in Guangzhou city, China. *Chemosphere* **2007,** *67*, (3), 614-622.
6. Zhang, Y. X.; Schauer, J. J.; Zhang, Y. H.; Zeng, L. M.; Wei, Y. J.; Liu, Y.; Shao, M., Characteristics of particulate carbon emissions from real-world Chinese coal combustion. *Environmental Science & Technology* **2008,** *42*, (14), 5068-5073.
7. WHO, *WHO Air quality guidlelines for particulate matter, ozone, nitrogen dioxide and sulfur dioxide*, World Health Organization, 2005.
8. Y. L. Sun, G. S. Zhuang, W. Ying, L. H. Han, J. H. Guo, D. Mo, W. J. Zhang, Z. F. Wang and Z. P. Hao, *Atmospheric Environment*, 2004, **38**, 5991-6004.

Table 6 Seasonal PM Mass and T tests



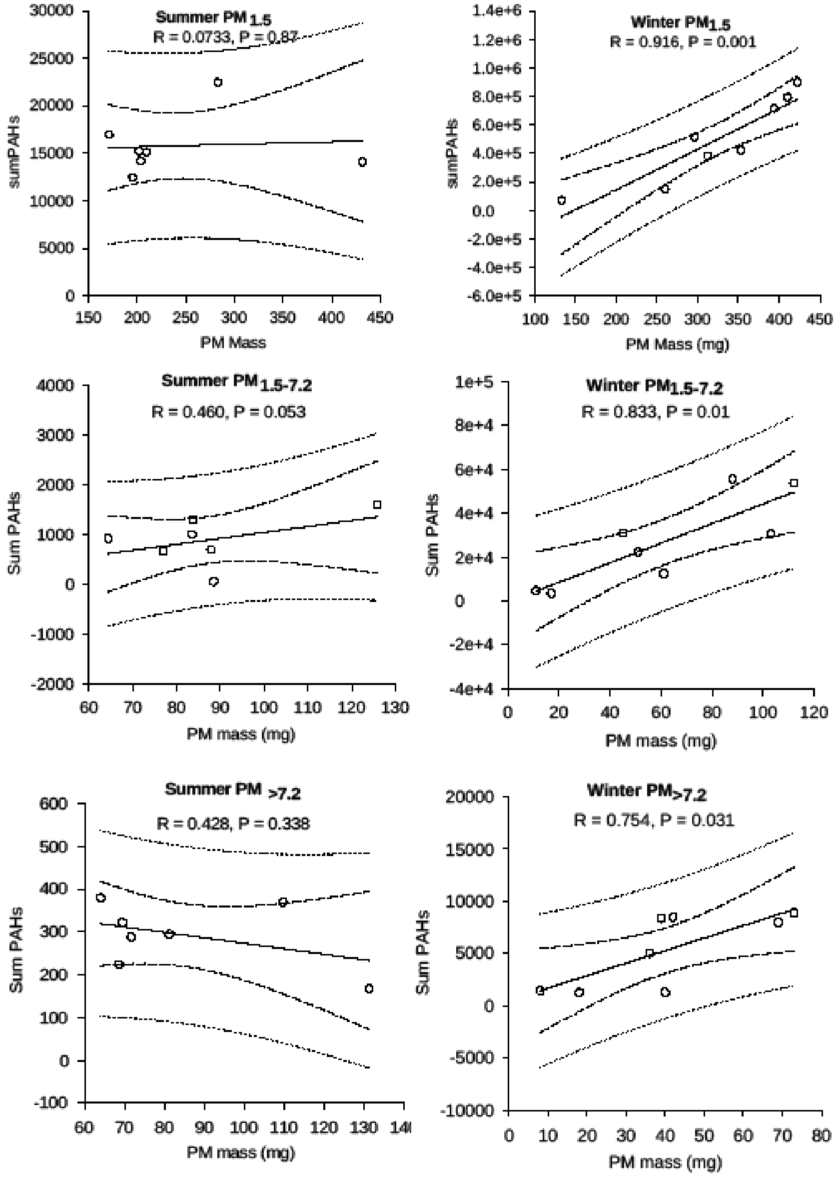
24 h Particulate Matter Mass Concentrations µg m^{-3}

PM Mass	**$PM_{1.5}$**			**$PM_{1.5-7.2}$**			**$PM_{7.2*}$**		**PM_{10}**		
Season:	Mean	t	p-value	Mean	t	p-value	Median	p-value	Mean	t	p-value
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-value Student's T test or *Mann-Whitney Rank Sum if normality failed, $PM_{10} = \Sigma PM_{1.5} + PM_{1.5-7.2}$

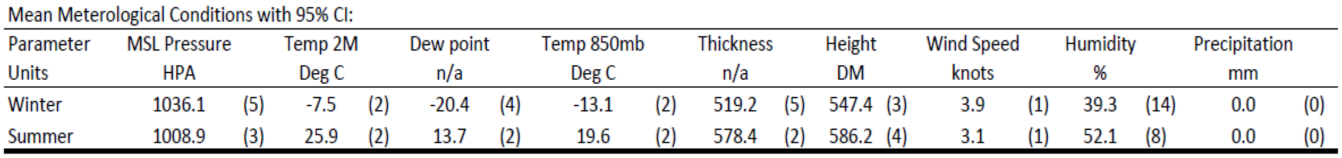
Table shows no significant difference (p-value > 0.05) between summer (N=7) and winter (N=8) PM mass for $PM_{1.5}$ and PM_{10}, but reflects a significant difference for $PM_{1.5-7.2}$ and $PM_{7.2}$.

Figure 1 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 the p-value < 0.05.

Table 7 Mean meteorological parameters (95%CI) obtained by NOAA ARL with GDAS1 archived data (**http://www.ready.noaa.gov/ready/amet.html**).



Mean Meterological Conditions with 95% CI:

Parameter	MSL Pressure		Temp 2M		Dew point		Temp 850mb		Thickness		Height		Wind Speed		Humidity		Precipitation	
Units	HPA		Deg C		n/a		Deg C		n/a		DM		knots		%		mm	
Winter	1036.1	(5)	-7.5	(2)	-20.4	(4)	-13.1	(2)	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)	19.6	(2)	578.4	(2)	586.2	(4)	3.1	(1)	52.1	(8)	0.0	(0)

Data was retrieved after converting sampling times into GMT for Beijing, China (lat 39.9, long 116.4). Data was collected by NOAA every 3 hours at 500mb, unless otherwise specified, and averaged for each 24 hour sample period. Values in the table represent the mean data over the sample period. It is noteworthy that a recent PM study from Beijing applied a humidity correction to PM mass measurement. Wang et al observed a large spread of relative humidity (40-90%)[9], 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 would result in 1 +/-3 $\mu g/m^3$ change in PM mass[9].

Reference:

[9] W. T. Wang, T. Primbs, S. Tao and S. L. M. Simonich, *Environmental Science & Technology*, 2009, **43**, 5314-5320.