1 **Supplementary Material**

2 **Polycyclic aromatic hydrocarbons with molecular weight 302 in**

3 **PM2.5 at two industrial sites of South China**

4 Shilong Wei[1,2], Ming Liu[1,2], Bo Huang[1,2], Xinhui Bi[1,*], Guoying Sheng[1], Jiamo Fu[1,3]

5

6 1. State Key Laboratory of Organic Geochemistry, Guangdong Province Key Laboratory of

7 Utilization and Protection of Environmental Resource, Guangzhou Institute of Geochemistry,

8 Chinese Academy of Sciences, Guangzhou, 510640, P.R. China

9 2. Graduate University of Chinese Academy of Sciences, Beijing 100039, P. R. China

10 3. School of Environmental and Chemical Engineering, Shanghai University, Shanghai

11 200444, P. R. China

12

13 *Corresponding author: Xinhui Bi

14 E-mail: bixh@gig.ac.cn

15

16 Tel: +86-20-85290195

17 Fax: +86-20-85290288

18

19 **1. Materials and Methods**

20 *1.1 Reagents*

21   Sixteen priority PAHs (16 compounds specified on EPA Method 610) in a mixture and

22 surrogate consisting of naphthalene-d8; acenaphthene-d10; phenanthrene-d10; chrysene-d12

23 and perylene-d12 standards were obtained from Cambridge Isotope Laboratories, Inc.

24 Hexamethylbenzene, and coronene-d12 were acquired initially as a solid from Aldrich

25 Chemical.

26   Five high molecular weight (HMW) PAH isomers, including dibenzo[a,e]fluoranthene

27 (DBaeF), dibenzo[a,l]pyrene (DBalP), dibenzo[a,e]pyrene (DBaeP), dibenzo[a,i]pyrene

28 (DBaiP), dibenzo[a,h]pyrene (DBaeP) were obtained from AccuStandard, Inc and Acros

29 Organics. There are 14 other isomer compounds that were also quantified by using the

30 average response factors (Schubert et al., 2003) including dibenzo[b,e]fluoranthene (DBbeF),

31 naphtho[1,2-b]fluoranthene (N12bF), naphtho[1,2-k]fluoranthene (N12kF),

32 dibenzo[b,k]fluoranthene (DBbkF), dibenzo[a,k]fluoranthene (DBakF),

33 dibenzo[j,l]fluoranthene (DBjlF), naphtho[1,2-e]pyrene (N12eP), naphtho[2,3-k]fluoranthene

34 (N23kF), naphtho[1,2-a]pyrene (N12aP), naphtho[2,3-e]pyrene (N23eP),

35 naphtha[2,1-a]pyrene (N21aP), dibenzo[e,l]pyrene (DBelP), naphtho[2,3-a]pyrene (N23aP),

36 benzo[b]perylene (BbPer).

37

38 *1.2 Extraction*

39   Prior to extraction, deuterated surrogate standards consisting of naphthalene-d8,

40   acenaphthylene-d10, phenanthrene-d10, chrysene-d12, perylene-d12, and dibenzo[a,i]-

41   pyrene-d14 were spiked onto the filters.   Filters were extracted with 60 mL dichloromethane

42   (DCM) using ultrasonic agitation under 30 ^{o}C and filtered.   The procedure was repeated

43   three times.   The combined extracts were filtered and concentrated by rotary evaporation

44   under vacuum.   Each sample was concentrated to about 0.5 mL.   Interfering compounds

45   were removed by liquid-solid chromatography using 2:1 silica-alumina column.   Two

46   fractions were eluted.   Fraction I (40mL of hexane) contained the aliphatic hydrocarbons,

47   while fraction II (100mL of DCM-hexane (1:1)) contained the priority PAHs and HMW

48   PAHs.   Then under a gentle stream of nitrogen the samples were reduced almost to dryness

49   and redissolved with n-hexane.   Internal standards hexamethylbenzene (for priority PAHs)

50   and coronene-d12 (for HMW PAHs) was added at this point.

51

52   *1.3. Instrumental Analysis*

53   All samples were analyzed using gas chromatography with mass selective detection

54   (GC/MS).   For priority PAHs analysis, the mass spectrometer used electron impact

55   ionization (EI) and selected ion monitoring (SIM) mode.   A DB-17MS capillary column (60

56   m × 0.25 mm × 0.25 μm) was used.   The chromatographic conditions were as follows:

57   injector temperature was 290 ^{o}C and detector temperature was 220 ^{o}C.   The temperature

58   ramp was: an initial oven temperature of 60 ^{o}C maintained for 5min, and increased at 6 ^{o}C

59   min^{-1} to a maximum of 300 ^{o}C for 45 min.   Helium was the carrier gas at a flow rate of 1.0

60   mL min^{-1}.

61   For nineteen PAH isomers with MW 302 were quantified with MS operated in electron

62   impact ion (EI) mode and selected ion monitoring (SIM).   GC was equipped with a

63   DB-17MS capillary column (60 m × 0.25 mm × 0.25 μm).   The chromatographic conditions

64   were as follows: injector temperature was 290 ^{o}C and detector temperature was 230 ^{o}C.   The

65   temperature ramp was: isothermal at 100 ^{o}C for 1 min, with 45 ^{o}C/min to 200 ^{o}C, with 2

66   ^{o}C/min to 310 ^{o}C, isothermal at 310 ^{o}C for 75 min, then with 45 ^{o}C/min to 320 ^{o}C, isothermal

67   at 320 ^{o}C for 10 min.   The helium was chosen as carrier gas (at a flow rate of 1.2 mL/min).

68   Chromatographic peaks of samples were identified based on the molecular ions and

69   retention times.   Concentrations of individual PAH isomers were quantified using the

70   corresponding deuterated internal standard.   The relative response factors to the internal

71   standard were calculated with the 8-point calibration curve method.

72

73   *1.4. Quality control (QC) and quality assurance (QA)*

74   Field blanks, which accompanied the field samples to the sampling sites, were used to

75   determine any background contamination.   Solvent blanks were analyzed.   The

76   concentrations of target compounds in the blanks were under the instrument detection.

77   Therefore, the results were not corrected for field blanks.   In addition, surrogate standards

78   were added to all the samples (including QA samples) to monitor procedural performance and

79 matrix effects. The mean recovery of dibenzo[a,i]pyrene-d14 for the HMW PAHs was

80 79.9%.

81

82　　　　　　　　Table S1. Meteorological parameters, PM2.5 and EC during sampling period

Date	Temperature (°C)	Humidity (%)	Wind speed (m s^{-1})	PM2.5(site A) (μg m^{-3})	PM2.5 (site B) (μg m^{-3})	EC(site A) (μg m^{-3})	EC(site B) (μg m^{-3})
Summer							
Aug 5 Day	28	87	3.6	24.2	28.2	1.90	1.42
Aug 5 Night	27	91	3.6	26.4	29.3	1.05	1.43
Aug 6 Day	26	91	2.5	29.8	32.6	2.25	1.85
Aug 6 Night	26	94	0.8	40.6	63.9	2.92	2.98
Aug 7 Day	34	60	3.6	46.6	37.6	2.93	1.32
Aug 7 Night	30	72	2.4	49.5	47.0	1.91	3.06
Aug 8 Day	33	61	3.5	49.4	32.6	3.09	1.25
Aug 8 Night	30	70	2.6	32.8	35.8	0.92	1.95
Aug 9 Day	33	62	2.5	41.5	25.2	2.50	1.22
Aug 9 Night	28	83	0.7	37.3	70.9	0.98	4.94
Aug 10 Day	34	57	2.2	41.4	41.1	2.08	2.13
Aug 10 Night	30	71	2.7	39.3	51.1	1.00	1.98
Aug 11 Day	32	66	1.7	50.9	111	2.17	2.67
Aug 11 Night	27	89	2.2	34.9		1.16	
Aug 12 Day	28	86	1.4	42.3		1.66	
Aug 12 Night	26	90	1.1	60.6	50.9	2.31	1.24
Aug 13 Day	29	79	2.4	64.8	65.0	2.80	2.26
Aug 13 Night	28	86	1.9	80.5	67.8	3.63	3.34
Aug 14 Day	29	83	2.4	72.2	50.7	1.93	2.25
Aug 14 Night	27	92	0.9	66.5	86.3	2.74	3.69
Aug 15 Day	32	68	2.2	74.4	52.8	1.90	2.19
Aug 15 Night	29	83	0.6	97.5	80.5	2.80	2.91
Aug 16 Day	33	62	2.6	58.4	57.1	1.54	2.43
Aug 16 Night	30	77	2.2	50.7	62.8	1.53	1.08
Winter							
Jan 24 Night	10	95	2.0	53.6	52.1	3.48	1.78
Jan 25 Day	15	73	7.4	68.4	40.4	1.71	1.19
Jan 25 Night	11	74	6.2	44.2	51.9	0.71	0.95
Jan 26 Day	14	63	2.6	81.1	77.0	1.90	1.18
Jan 26 Night	13	79	0.9	131	147	5.97	3.73
Jan 27 Day	14	91	0.9	163	200	7.08	4.46
Jan 27 Night	14	97	1.1	164	148	9.57	5.58
Jan 28 Day	19	82	1.9	138	140	6.24	4.38
Jan 28 Night	18	92	2.0	199	266	6.97	7.43
Jan 29 Day	20	88	1.9	185	185	7.12	5.95
Jan 29 Night	18	86	2.4	142	114	4.91	4.62
Jan 30 Day	20	75	1.6	188	179	4.88	4.38
Jan 30 Night	20	84	1.7	160	131	7.06	4.60

Jan 31 Day	22	78	1.4	178	112	5.15	3.13
Jan 31 Night	20	86	1.3	142	108	6.44	4.76
Feb 1 Day	21	78	2.0	97.1	117	2.80	2.92
Feb 1 Night	19	78	2.9	88.6	101	2.69	4.04
Feb 2 Day	20	81	2.0	139	89.5	6.21	3.21
Feb 2 Night	19	88	3.3	83.2	93.2	4.34	3.91
Feb 3 Day	14	93	3.1	44.1	51.8	3.35	1.80
Feb 3 Night	13	94	3.8	22.5	23.5	1.63	1.28

83

84

85

Table S2. The p values for non-parametric Mann-Whitney U test

Compounds	Sites A and B	Summer and winter		Day and night	
		Site A	Site B	Site A	Site B
DBbeF	0.026	0.000	0.002	0.570	0.041
N12bF	0.008	0.000	0.001	0.496	0.007
N12kF	0.004	0.000	0.000	0.555	0.006
DBaeF	0.011	0.000	0.001	0.570	0.004
DBbkF	0.008	0.000	0.001	0.633	0.001
DBakF	0.000	0.000	0.001	0.803	0.016
DBjlF	0.010	0.000	0.003	0.547	0.114
N12eP	0.009	0.000	0.003	0.335	0.061
DBalP	0.004	0.000	0.014	0.820	0.000
N23kF	0.000	0.000	0.003	0.768	0.003
N12aP	0.002	0.000	0.001	0.510	0.025
N23eP	0.018	0.000	0.001	0.266	0.035
DBaeP	0.010	0.000	0.002	0.716	0.003
N21aP	0.004	0.000	0.000	0.602	0.065
DBelP	0.183	0.000	0.002	0.658	0.181
N23aP	0.001	0.000	0.036	0.928	0.000
BbPer	0.001	0.000	0.003	0.666	0.003
DBaiP	0.001	0.000	0.003	0.838	0.026
DBahP	0.006	0.000	0.001	1.000	0.269

86

87

88

89 Table S3. Mean concentrations of four highly carcinogenic MW302 isomers (pg m^{-3})

City	Source	DBalP	DBaeP	DBaiP	DBahP	Reference
Qingyuan, China	PM2.5	79	314	164	79	This study
Beijing, China	PM1.5	~1500	~15000	~5000	~2500	1
Stockholm, Sweden	Air particle	3.39	23.7	5.52	1.86	2
Boston USA	Air particle		133			3
Riverside, USA	Air particle		2.7	< 0.5	< 0.5	4
Oporto, Portugal	PM2.5/PM10	15.8/19.8				5

90

91

92   Table S4. Average concentrations of PM2.5-bound priority PAHs (ng m^{-3})

Compounds	Summer		Winter	
	Site A	Site B	Site A	Site B
acenaphthylene	0.02	0.03	0.06	0.05
acenaphthene	0.01	0.01	0.01	0.01
fluorene	0.04	0.05	0.09	0.10
phenanthrene	0.22	0.31	1.47	1.43
anthracene	0.04	0.05	0.10	0.05
fluoranthene	0.56	0.45	4.80	3.43
pyrene	0.81	0.55	4.45	2.09
benz[a]anthracene (BaA)	0.40	0.21	2.01	0.82
Chrysene (Chry)	0.76	0.42	4.07	2.22
benzo[b]fluoranthene (BbF)	1.75	1.08	11.2	7.19
benzo[k]fluoranthene (BkF)	0.81	0.44	5.10	2.36
benzo[a]pyrene (BaP)	1.64	0.69	7.50	3.07
indeno[cd]pyrene (IcdP)	5.72	2.41	22.7	12.6
dibenzo[ah]anthrathene (DBahA)	0.87	0.51	4.62	2.65
benzo[ghi]perylene	8.42	3.33	30.8	16.1
$\sum$PAHs	22.0	10.5	98.9	54.1

93

94
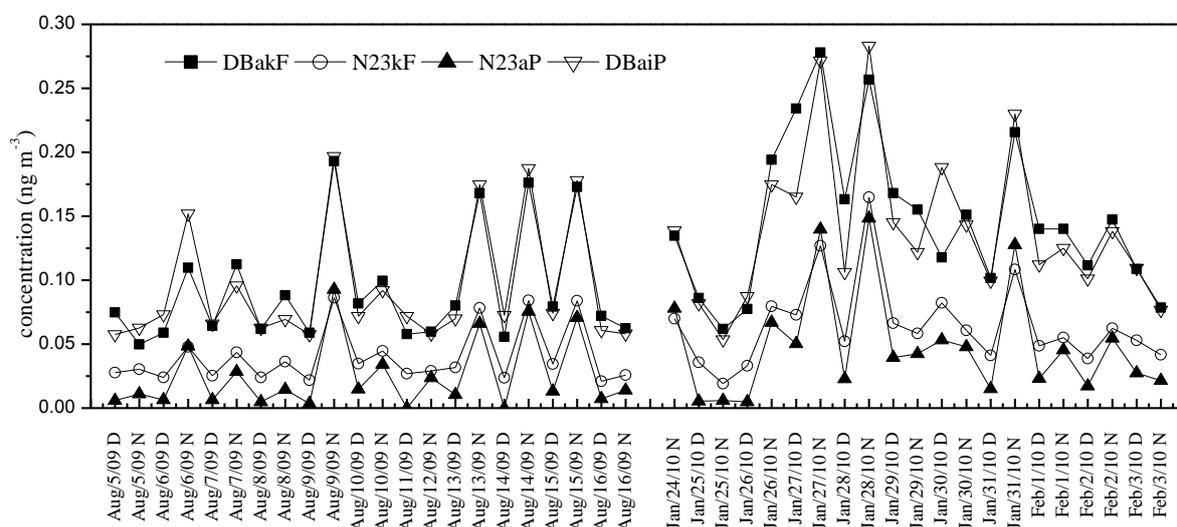
95

96   Figure S1. The diurnal variation of DBakF, N23kF, N23aP and DBaiP at site B

97

98

99   **References**

100   1. J. Layshock, S.M. Simonich and K.A. Anderson, *J. Environ. Monit.*, 2010, 12, 2290-2298.

101   2. C. Bergvall and R. Westerholm, *Environ. Sci. Technol.*, 2007, 41, 731-737.

102   3. J.O. Allen, J.L. Durant, N.M. Dookeran, K. Taghizadeh, E.F. Plummer, A.L. Lafleur,   A.F.

103   Sarofim and K.A. Smith, *Environ. Sci. Technol.*, 1998, 32, 1928-1932.

104   4. R. Krieger and J. Wright, 1997. Ambient monitoring of selected PAHs in California, Air

105   and Waste Management Association 90th Annual Meeting and Exhibition, Ontario.

106   5. D. Castro, K. Slezakova, M.T. Oliva-Teles, C. Delerue-Matos, M.C. Alvim-Ferraz, S.

107   Morais, and M.C. Pereira, *J. Sep. Sci.*, 2009, 32, 501-510.

108