Supplemental Information

Long-Term and Seasonal Changes in Sources of Urban Atmospheric Particulates in The Western Pacific

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Text 1. Determination of PAHs and NPAHs

An area of each quartz fiber filter containing atmospheric total suspended particulate matter (TSP) was cut into small pieces in a glass flask, and an internal standard solution including Pyr-d_{10}, 1-NP-d_9 and 2-fluoro-7-nitrofluorene (FNF) was added. PAHs, NPAHs and internal standards were extracted with benzene/ethanol (3:1, v/v), and the organic solution was successively washed with diluted solutions of sodium hydroxide and sulfuric acid, and finally with distilled water. After the organic solution was evaporated to dryness, the residue was dissolved in a small volume of ethanol. The solution was used for high-performance liquid chromatographic (HPLC) quantification of PAHs and NPAHs.

Nine PAHs, fluoranthene (FR), pyrene (Pyr), benz[*a*]anthracene (BaA), chrysene (Chr), benzo[*b*]fluoranthene (BbF), benzo[*k*]fluoranthene (BkF), benzo[*a*]pyrene (BaP), benzo[*ghi*]perylene (BghiPe) and indeno[1,2,3-*cd*]pyrene (IDP), were quantified using an HPLC equipped with a fluorescence detector (Shimadzu LC10A series). The analytical column was a reversed phase column (Inertsil ODS-P, 4.6 i.d. × 250 mm, GL Science Inc., Tokyo, Japan). The mobile phase was a mixture of acetonitrile/water. The time program for fluorescence detection was set at the optimum excitation and emission wavelengths. HPLC conditions were according to the United States Environmental Protection Agency methods [1] with several modifications. Pyr-d_{10} was used as the internal standard for the quantification.

Six NPAHs, 9-nitroanthracene (9-NA), 1-nitropyrene (1-NP), 6-nitrocrysene (6-NC), 7-nitrobenz[*a*]anthracene (7-NBaA), 3-nitroperylene (3-NPer) and 6-nitrobenzo[*a*]pyrene (6-NBaP), were quantified using an HPLC equipped with a reducing column packed with platinum/rhodium and a chemiluminescence detector. The analytical columns were reversed-phase columns (Cosmosil 5C18-MS-II, 4.6 i.d. (250 + 150) mm, Nacalai Tesque, Kyoto, Japan). The mobile phase was a mixture of an imidazole buffer and acetonitrile. The chemiluminescence reagent solution was an acetonitrile solution containing bis(2,4,6-trichlorophenyl)oxalate and hydrogen peroxide. 1-NP-d_9 and FNF were used as internal standards for quantification. More detailed HPLC conditions were described in our previous reports with limits of quantification [2-4]. The recoveries of NPAHs varied between 87% and 104%, with limits of detection (S/N = 3) that varied between 0.25 and 1.5 fmol, and limits of quantification (S/N = 10) that varied between 10^{-15} and 10^{-12} (over two orders of magnitude).[5]

Figure S1. Sampling cities in Western Pacific Ocean.

Table S1. Characteristics of the sampled cities.

City	**Location** **Latitude, Longitude**	Population	Avg. temp. (°C) Summer	 Winter	Characteristics
Sapporo	**36°33′N, 136°40′E**	1,970,000	22.3	−3.6	Capital of Hokkaido prefecture, Japan; Commercial city
Kanazawa	36°33′N, 136°40′E	460,000	27.0	3.8	Capital of Ishikawa prefecture, Japan; Commercial city
Tokyo	36°33′N, 136°40′E	1,400,000	26.4	5.2	Capital of Japan; Biggest city in Japan; Commercial city
Sagamihara	36°33′N, 136°40′E	270,000	26.7	5.9	Satellite city of Tokyo; Commercial city
Kitakyushu	33°53′N, 130°53′E	940,000	27.4	5.8	Industrial city (Iron manufacture)
Shenyang	41°37′N, 123°25′E	8,250,000	24.6	−12.0	Capital of Liaoning province, China; Commercial city; Coal heating in winter
Beijing	39°54′N, 116°24′E	21,700,000	25.8	−4.6	Capital of China; Commercial city; Coal heating in winter
Shanghai	31°13′N, 116°24′E	24,300,000	27.8	3.5	Economic and financial center of China, Commercial city

Vladivostok	43°06′N, 131°52′E	630,000	21.2	−12.1	Capital of Primorsky Krai, Russia; Port city
Busan	35°06′N, 129°02′E	3,490,000	25.9	3.2	Second biggest city in Korea; Port city

Table S2. Atmospheric concentrations of TSP, 1-NP and Pyr in 10 cities from 1997 to 2018.

Year/Season[c]	**[TSP], μgm^{-3}**	**[1-NP], fmol m^{-3}**	**[Pyr], pmol m^{-3}**
	Sapporo		
1997S	ND[b]	120	0.99
1997W	ND[b]	570	5.1
2004S	33	22	0.65
2005W	23	94	2.1
2007S	34	20	0.32
2008W	32	150	4.3
2010S	37	11	0.25
2010W	29	72	2.7
2013S	15	3.6	0.19
2014W	13	43	1.0
	Kanazawa		
1997S	ND[2]	180	1.0
1997W	ND[b]	480	2.9
1999S	34	180	1.2
1999W	56	480	2.5
2004S	31	91	0.82
2005W	29	97	1.0
2007S	39	42	0.53
2008W	24	51	1.7
2010S	28	15	0.4
2010W	28	43	1.5
2013S	42	18	0.54
2014W	34	26	2.0
2017S	18.2	6.0	0.40
2018W	21.6	11.9	1.07
	Tokyo		
1997S	ND[b]	48	0.78
1997W	ND[b]	280	3.3
2004S	29	22	0.52
2005W	31	46	1.2
	Sagamihara		
2007S	46	15	0.44
2008W	21	25	1.1
2010S	34	5.3	0.09
2010W	35	35	1.4
2013S	42	5.8	1.3
2014W	39	25	1.5
	Kitakyushu		
1997S	ND[b]	16	1.5
1997W	ND[b]	55	2.8
2004S	40	22	3.0
2005W	38	70	2.0
2007S	29	5.2	0.22
2008W	27	29	2.0
2010S	24	13	0.88
2010W	52	37	2.2
2013S	20	1.9	0.30
2014W	21	31	8.7

		Shenyang	
2001S	114	150	3.0
2002W	194	720	250
2007S	151	170	7.5
2008W	171	790	74
2010S	177	96	2.7
2010W	171	730	37
2013S	88	90	6.0
2014W	178	760	110
		Beijing	
2004W	171	740	170
2007S	757	78	4.9
2008W	211	680	100
2010S	96	48	2.5
2010W	207	440	290
2013S	125	32	2.4
2014W	667	260	81
		Shanghai	
2007S	84	150	1.1
2007W	107	150	2.9
2010S	81	34	0.75
2010W	154	200	5.6
2013S	34	19	0.74
2014W	128	170	13
2015S	ND[d]	7.7	1.1
2015W	ND[d]	47	5.4
2017S	ND[d]	17	0.54
2018W	ND[d]	36	4.2
		Vladivostok	
1999S	ND[d]	17	0.49
1999W	ND[d]	460	24
2005W	ND[d]	290	16
2007S	95	19	0.86
2008W	80	350	26
2010S	41	19	1.0
2010W	73	340	52
2013S	50	6.0	0.27
2014W	80	150	8.1
		Busan	
2005W	44	84	2.5
2007S	62	20	0.37
2008W	39	91	4.0
2010S	34	12	0.54
2010W	50	56	5.2

[c]Season: S, Summer; W, Winter. [d]ND: No data. Atmospheric concentrations of TSP, 1-NP and Pyr were cited from our previous reports [5-7].

Table S3 x and y values for 10 cities from 1997 to 2018.

Year/ Season	*x*	*y*
	Sapporo	
1997 S	0.903	-
1997 W	0.893	-
2004 S	0.651	0.015
2005 W	0.721	0.084
2007 S	0.795	0.011
2008 W	**0.659**	**0.105**
2010 S	0.716	0.006
2010 W	0.590	0.061
2013 S	0.491	0.007
2014 W	0.710	0.069
	Kanazawa	
1997 S	0.948	-
1997 W	0.940	-
1999 S	0.929	0.087
1999 W	0.954	0.199
2004 S	0.891	0.050
2005 W	0.871	0.058
2007 S	0.837	0.020
2008 W	0.618	0.050
2010 S	0.680	0.012
2010 W	0.543	0.041
2013 S	0.644	0.010
2014 W	0.385	0.027
2017 S	0.492	0.018
2018 W	0.343	0.033
	Tokyo	
1997 S	0.792	-
1997 W	0.850	-
2004 S	0.758	0.014
2005 W	0.776	0.027
	Sagamihara	
2007 S	0.639	0.007
2008 W	0.884	0.020
2010 S	0.763	0.002
2010 W	0.559	0.026
2013 S	0.141	0.009
2014 W	0.454	0.020
	Kitakyushu	
1997 S	0.341	-
1997 W	0.506	-
2004 S	0.239	0.029
2005 W	0.659	0.041
2007 S	0.557	0.005
2008 W	0.425	0.035
2010 S	0.425	0.018
2010 W	0.460	0.022
2013 S	0.208	0.001
2014 W	0.105	0.134
	Shenyang	
2001 S	0.745	0.026
2002 W	0.075	0.405
2007 S	0.545	0.030
2008 W	0.341	0.182
2010 S	0.666	0.012
2010 W	0.506	0.121
2013 S	0.425	0.034
2014 W	0.227	0.231
	Beijing	

2004 W	0.138	0.334
2007 S	0.443	0.003
2008 W	0.223	0.177
2010 S	0.491	0.014
2010 W	0.008	0.420
2013 S	0.390	0.009
2014 W	0.088	0.039
	Shanghai	
2007 S	0.918	0.030
2007 W	0.754	0.028
2010 S	0.721	0.009
2010 W	0.666	0.029
2013 S	0.580	0.014
2014 W	0.385	0.020
2015 S	0.233	-
2015 W	0.284	-
2017 S	0.637	-
2018 W	0.278	-
	Vladivostok	
1999 S	0.659	-
1999 W	0.491	-
2005 W	0.476	-
2007 S	0.533	0.005
2008 W	0.385	0.156
2010 S	0.491	0.013
2010 W	0.214	0.264
2013 S	0.533	0.004
2014 W	0.491	0.054
	Busan	
2005 W	0.651	0.043
2007 S	0.762	0.006
2008 W	0.545	0.062
2010 S	0.533	0.010
2010 W	0.341	0.044

x (= [P_h]/[P_c]) and y (= [P_c]/[TSP]) were calculated from Table S2 by equations (i) and (ii) in the text. Blank means not calculated.

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