

Recent Changes in Atmospheric Polycyclic Aromatic Hydrocarbons (PAHs) and Nitropolycyclic Aromatic Hydrocarbons (NPAHs) in Shenyang, China

著者	Tang Ning, Tokuda Takahiro, Izzaki Akihiko, Tamura Kenji, Ji Ruonan, Zhang Xuemei, Dong Lijun, Kameda Takayuki, Toriba Akira, Hayakawa Kazuichi
journal or publication title	Environmental Forensics
volume	12
number	4
page range	342-348
year	2011-12-01
URL	http://hdl.handle.net/2297/31957

doi: 10.1080/15275922.2011.622347

1 Recent Changes in Atmospheric Polycyclic Aromatic Hydrocarbons and Nitropolycyclic
2 Aromatic Hydrocarbons in Shenyang, China

3

4

5 Ning Tang,¹ Takahiro Tokuda,¹ Akihiko. Izzaki,¹ Kenji Tamura,² Ruonan, Ji,³ Xuemei Zhang,³
6 Lijun Dong,³ Takayuki Kameda,¹ Akira Toriba,¹ and Kazuichi Hayakawa¹

7

8

9 ¹*Graduate School of Natural Science and Technology, and Institute of Medical,*
10 *Pharmaceutical and Health Sciences, Kanazawa University, Kakuma-machi, Kanazawa*
11 *920-1192, Japan*

12 ²*National Institute for Environmental Studies, 16-2 Onogawa, Tsukuba 305-8506, Japan*

13 ³*Division of Science & Education, Shenyang Center for Disease Control and Prevention, No.*
14 *37 Qishang Road, Huanggu District, Shenyang, China*

15

16

17 *To whom correspondence should be addressed:

18 phone: +81 76 234 4458 fax: +81 76 234 4456

19 E-mail address: tou@p.kanazawa-u.ac.jp (N. Tang)

20

21

22 Key words: Polycyclic aromatic hydrocarbon, Nitropolycyclic aromatic hydrocarbon,
23 1-Ntropyrene/pyrene ratio ([1-NP]/[Pyr]), Air pollution, Shenyang government Blue Sky
24 Project.

1 Abstract

2

3 Airborne particulates were collected in three size fractions by using Anderson low-volume
4 air samplers in Shenyang, China in winter and summer in 2007. Compared with data obtained
5 in 2001 at the same sites, the total concentrations of nine polycyclic aromatic hydrocarbons
6 (PAHs) in winter decreased by 67% at one site and decreased by 40% at the other site, while
7 the total concentrations of four nitropolycyclic aromatic hydrocarbons (NPAHs) did not
8 decrease. This suggests that environmental countermeasures begun in 2001 were effective in
9 decreasing the concentration of PAHs. However, in summer, the concentrations of PAHs and
10 NPAHs rose by the factors of 4 and 5, respectively, possibly because of an increase in the
11 number of motor vehicles.

12

13

14

15

16

17

18

19

20

21

22

23

24

1 **Introduction**

2

3 Many polycyclic aromatic hydrocarbons (PAHs) and nitropolycyclic aromatic
4 hydrocarbons (NPAHs) are carcinogenic and/or mutagenic. The International Agency for
5 Research on Cancer has ranked benzo[*a*]pyrene (BaP) in Group 1 (carcinogenic to humans)
6 and 1-nitropyrene (1-NP) in Group 2A (probably carcinogenic to humans) (IARC, 2005).
7 Several PAHs also have estrogenic/antiestrogenic or antiandrogenic activities (Kizu et al.,
8 2000). Atmospheric PAHs such as BaP and NPAHs such as 1-NP mainly originate from
9 imperfect combustion and pyrolysis of organic matters (Hayakawa et al., 1995a; Rogge et al.,
10 1993). In addition, some NPAHs, such as 2-NP, are formed in the atmosphere via reactions of
11 their parent PAHs and NO₂ (Arey et al., 1986). We previously reported that the main
12 contributors to atmospheric PAHs and NPAHs were automobiles in Japanese and South
13 Korean commercial cities (Sapporo, Kanazawa, Toyama, Tokyo and Seoul) (Kakimoto et al.,
14 2000, 2002; Hayakawa et al., 2000, 2002; Tang et al., 2002a, 2005), while they were coal
15 combustion systems in Chinese and Far-eastern Russian cities (Beijing, Shenyang, Fushun,
16 Tieling and Vladivostok) (Hattori et al., 2007; Hayakawa et al., 2007; Tang et al., 2002a,
17 2005, 2009).

18 During the past three decades, large increases in the consumption of petroleum and coal in
19 China have led to air pollution. Shenyang city is the economic center of northeast China. The
20 main sources of air pollution in Shenyang are exhausts from domestic heating, industry and
21 motor vehicles. In 2001 - 2002, the average concentrations of total PAHs (9 kinds of PAHs)
22 and NPAHs (7 kinds of NPAHs) in Shenyang were 534 pmol m⁻³ and 677 fmol m⁻³,
23 respectively (Hattori et al., 2007). These concentrations were significantly higher than those
24 in Kanazawa, Japan in the same period. To reduce air pollution, the Shenyang government
25 undertook the Blue Sky Project (<http://www.syepb.gov.cn/>), in which 100 factories were

1 transferred to the outer city, and 5,000 inefficient boilers for domestic heating were removed
2 between 2001 to 2007. These changes helped to reduce the annual average concentrations of
3 PM₁₀ from 190 μg m⁻³ in 2001 to 120μg m⁻³ in 2009 (<http://www.syepb.gov.cn/>).

4 In this study, airborne particulates (APs) were collected by using the same method and at
5 the same sites as our previous investigation in 2007 (Hattori et al., 2007). Our objectives were
6 to clarify the effect of the above countermeasures and to understand the present pollution
7 status of PAHs and NPAHs in Shenyang, China.

8

9 **Materials and Methods**

10

11 *Sampling Sites*

12 Sampling sites in this study were the same as our previous study (Hattori et al., 2007).
13 SY-1 (Heping elementary school) was in a commercial area and SY-2 (Taishan elementary
14 school) was in a mixed residential and commercial area. Airborne particulates were collected
15 simultaneously at the two sites using Andersen low-volume air samplers (AN-200, Shibata
16 Sci. Tech., Tokyo, Japan) at a flow rate of 28.3 L min⁻¹. The height of the intake varied from
17 1 to 3 m above ground level. APs were separately collected only in three fractions according
18 to their aerodynamic size: larger than 7 μm, 2.1 ~ 7 μm and smaller than 2.1 μm onto quartz
19 fiber filters (2500QAT-UP, Pallflex Products, Putnam, CT, U. S. A.) different to our previous
20 study (Hattori et al., 2007; APs were collected in nine fractions and separated in same three
21 granulometric groups for PAHs and NPAHs analysis). Air samples were collected at two sites
22 on March 10 - 17 (winter) and September 17 - 24, 2007 (summer). Filters were replaced every
23 day. At each site, seven 3-layer filters were used for each of the above sampling periods. The
24 filters were dried in a desiccator in the dark, weighed and stored at -20°C until use.

25

1 *Chemicals*

2 USEPA 610 PAHs mix, a mixture of 16 PAHs including fluoranthene (FR), pyrene (Pyr),
3 benz[*a*]anthracene (BaA), chrysene (Chr), benzo[*b*]fluoranthene (BbF), benzo[*k*]fluoranthene
4 (BkF), BaP, benzo[*ghi*]perylene (BgPe) and indeno[1,2,3-*cd*]pyrene (IDP) were purchased
5 from Supelco Park (Bellefonte, PA, U. S. A). Two internal standards for PAHs (pyrene-*d*₁₀
6 (Pyr-*d*₁₀) and benzo[*a*]pyrene-*d*₁₂ (BaP-*d*₁₂)) were purchased from Wako Pure Chemicals
7 (Osaka, Japan). 1-NP, 6-nitrochrysene (6-NChr), 6-nitrobenzo[*a*]pyrene (6-NBaP) and an
8 internal standard for NPAHs (2-fluoro-7-nitrofluorene (FNF)) were purchased from Chiron
9 AS (Trondheim, Norway). All other chemicals used were of analytical reagent grade.

10

11 *Sample Treatment and Analytical Procedures*

12 Three-layer filters (larger than 7 μm, 2.1 ~ 7 μm, smaller than 2.1 μm) of each sample
13 were cut into small pieces and placed in a flask, respectively. By this treatment, the
14 concentrations of PAHs and NPAHs in the three groups were obtained for each sample. Both
15 PAHs and NPAHs were extracted ultrasonically twice with benzene/ethanol (3:1, v/v) and
16 then the solution was filtered with a 0.45μm membrane filter (HLC-DISK13, Kanto Chemical
17 CO.,INC., Tokyo, Japan). Internal standards, Pyr-*d*₁₀, BaP-*d*₁₂ and FNF, were added to the
18 flask prior to the ultrasonic extraction. In the case of PAHs, the filtrate was evaporated to
19 dryness. The residue was dissolved in 0.5 mL of acetonitrile, and then injected into the HPLC
20 system for PAHs. In the case of NPAHs, the filtrate was washed once with 5% (w/v) sodium
21 hydroxide solution, once 20% (v/v) sulfuric acid solution and twice water for removing acid
22 and base substance. Then the solution was evaporated to dryness with rotation evaporator.
23 The residue was dissolved in 1 mL of 75% ethanol-0.02 M acetic acid-sodium acetate buffer
24 (pH 5.5). The solution was filtered with a 0.45 μm HLC-Disk membrane filter (Kanto
25 Chemical Co., Inc., Tokyo, Japan), and an aliquot of this solution was injected into the HPLC

1 system for NPAHs. Other conditions were the same as in our previous reports (Hayakawa et
2 al., 1991; Tang et al., 2002b).

3 The nine PAH species were determined by using HPLC with fluorescence detection. The
4 PAH HPLC system consisted of a reversed-phase column (Inertsil ODS-P, 4.6 i.d. x 250 mm,
5 GL Sciences Inc., Tokyo, Japan) with an acetonitrile/water gradient and fluorescence
6 detection. The flow rate was 1 mL min⁻¹. The time program of the fluorescence detector was
7 set to detect at the optimum excitation and emission wavelengths for each PAH. Other
8 conditions were the same as in our previous report (Tang et al., 2002b).

9 The four NPAH species were determined by using HPLC with chemiluminescence
10 detection. The HPLC system consisted of two reversed-phase columns (Cosmosil 5C18-MS,
11 4.6 i.d. x (250 + 150) mm, Nacalai Tesque, Tokyo, Japan) connected in series with
12 chemiluminescence detection. The mobile phase was 10 mM imidazole buffer (pH
13 7.6)-acetonitrile (1:1, v/v), and the chemiluminescence reagent solution was an acetonitrile
14 solution containing 0.02 mM bis(2,4,6-trichlorophenyl)oxalate and 15 mM hydrogen peroxide.
15 The flow rate was 1 mL min⁻¹ for each solution. Other conditions were the same as in our
16 previous report (Hayakawa et al., 1991; Tang et al., 2003).

17

18 *Data Analysis*

19 The major sources of PAHs and NPAHs were identified by a cluster analysis with Ward's
20 method and standardized squared Euclidean distance. The statistical analysis software
21 program used in this study was kindly provided by Dr. Susumu Hayakari of Aomori
22 Prefectural Institute of Public Health and Environment (Aomori, Japan). For the cluster
23 analysis, we used the concentration ratios of 1-NP to Pyr, 6-NBaP to BaP and individual PAH
24 to total PAHs in the airborne particulates collected at two sites in 2001 - 2002 (Hattori et al.,
25 2007) and 2007. The data of Tokyo in summer in 2004 and in winter in 2005 were used

1 grouping (Tang et al., 2005). The data of average temperature, dew point and wind speed in
2 Shenyang during our sampling periods were obtained from USA National Climatic Data
3 Center (<http://lwf.ncdc.noaa.gov/oa/climate/onlineprod/drought/xmgr.html#gr>) and average
4 humidity were calculated by using the data of average temperature and dew point.

5

6 **Results and Discussion**

7

8 *Concentrations*

9 The PAH and NPAH concentrations were higher in winter than in summer at each site and
10 they were both higher at SY-1 than at SY-2 (Table 1). Measurements made in 2001 to 2002
11 showed similar increases in winter (Hattori et al., 2007).

12 Fig. 1 compares the total concentrations of nine PAHs and three NPAHs measured in the
13 two studies (One of NPAHs measured in the present study was not measured in the earlier
14 study). In winter, the concentrations of PAHs decreased by 40% at SY-1, which is in a
15 commercial area, and decreased by 67% at SY-2, which is in a more residential area (Fig. 1A).
16 However, the concentration of NPAHs did not change markedly at either site, which suggests
17 that Shenyang's Blue Sky Project was more effective against PAHs than NPAHs in winter.
18 On the other hand, in summer, the concentrations of PAHs and NPAHs rose by a factor of at
19 least 4 at both sites. A likely contributing factor was an increase in the number of motor
20 vehicles from 360,000 in 2000 to 560,000 in 2007 (<http://www.syepb.gov.cn/>).

21

22 *Distribution of PAHs, NPAHs and APs in Different Size Particulate Fractions*

23 The concentrations and compositions of air pollution matters are often affected by
24 meteorological conditions (Yamasaki et al., 1982). PAH, NPAH and AP concentrations were
25 found to be highly correlated with humidity at the two sites in summer (Table 2). However,

1 no such correlations were found with temperature or wind speed, possibly because of their
2 smaller ranges (15 - 22°C and 1.3 - 2.4 m s⁻¹) and because rainfall was only one-third the
3 normal amount during the summer sampling period. However, in winter, AP (> 7 µm) was
4 negatively correlated with humidity and positively correlated with wind speed at both sites.
5 Temperature also seemed to be positively correlated with PAH and NPAH levels in all size
6 fractions. These observations suggest that cold and dry air, which blows predominantly from
7 the inner Asian continent in winter, increased the concentrations of coarse particulates (> 2.1
8 µm) and decreased the concentrations of PAHs, NPAHs and fine particulates (< 2.1 µm) in
9 the atmosphere (Table 2).

10 The main sources of atmospheric PAHs and/or NPAHs in Shenyang in summer are
11 automobiles, while in winter they seem to be coal stoves and coal boilers used for domestic
12 heating (Tang et al., 2005; Hattori et al., 2007; Kong et al., 2010). In 2007, the percentages of
13 total PAHs and NPAHs in the fine particulate fraction, which is the fraction that most
14 adversely affects human health, were about 92% and 81%, respectively at both sites (Fig. 2),
15 in agreement with previous reports. (Hayakawa et al., 1995b; Kawanaka et al., 2004).
16 However, in 2002, the percentages of total PAHs and total NPAHs in the fine fraction were
17 70% and 60% of the total, respectively. In winter 2002, the coarse size particulates had high
18 PAH and NPAH levels (Fig. 2). In general, inefficient boilers contributed greatly to the large
19 size particulates in the atmosphere because of their imperfect combustion. Therefore, the
20 increase in the ratio of the total PAHs and total NPAHs in the fine fraction from 2002 to 2007
21 was probably due to the removal of about 5000 boilers by the Shenyang government.

22 However, the difference of atmospheric concentrations of NPAHs between 2002 and 2007
23 was not significant. According to our previous study, the concentrations of NPAHs in the
24 particulates collected in automobiles were significantly higher than those in coal combustion
25 systems. By contrast, the concentrations of PAHs were lower in automobiles (Hayakawa et al.,

1 2000; Tang et al., 2005). In addition, the particulate sizes originating from automobiles were
2 very small (Ho et al., 2006). These observations suggest that the increase in the number of
3 motor vehicles also contributed to the fine particulate fractions of PAHs and NPAHs,
4 especially the latter.

5

6 *Compositions and Main Sources*

7 Multivariate statistical analysis methods and several diagnostic ratios have been used to
8 identify possible emission sources of PAHs and NPAHs and to compare their compositions in
9 the atmosphere (Bourotte et al., 2005; Kakimoto et al., 2002; Rogge et al., 1993). The
10 compositions of PAHs and NPAHs were compared by a cluster analysis using Ward's method.
11 As parameters, we used the concentration ratios of 1-NP to Pyr, 6-NBaP to BaP and
12 individual PAHs to total PAHs in the airborne particulates collected at the two sites in 2001 -
13 2002 and 2007. The same compound pairs were investigated in Tokyo in summer in 2004 and
14 in winter in 2005 (Tang et al., 2005) and are used here as a reference. As shown in Fig. 3, two
15 large clusters were observed according to the compositions of PAHs and NPAHs at all sites.
16 Cluster 1 includes all winter samples collected at the two sites in Shenyang. All summer
17 samples collected at the two sites in Shenyang and summer and winter samples in Tokyo were
18 grouped into Cluster 2. This result indicates that the compositions of PAHs and NPAHs in
19 winter were different from the compositions in summer at the two sites in Shenyang and that
20 the compositions of PAHs and NPAHs in summer at these sites were similar to those in
21 Tokyo in both summer and winter. Previously, we reported that the main sources of
22 atmospheric PAHs and NPAHs were motor vehicles in all seasons in Tokyo, while they were
23 coal combustion systems in winter and motor vehicles and coal combustion systems in
24 summer in Shenyang (Tang et al., 2005; Hattori et al., 2007). These results suggest that the
25 major contributors of atmospheric PAHs and NPAHs in Shenyang did not change

1 significantly during 2001 - 2002 to 2007. However, the data in Cluster 1 in Fig. 3 indicate that
2 the compositions of PAHs and NPAHs in winter at the two sites in Shenyang slightly differed
3 between 2002 and 2007. Possible causes of the differences in 2007 include the air pollution
4 countermeasures and the increase in the number of vehicles.

5 The [1-NP]/[Pyr] ratio is a useful indicator for estimating the contributions of motor
6 vehicles and coal combustion systems to atmospheric PAHs and NPAHs (Tang et al., 2005).
7 Although 1-NP can form during the sampling and a part of Pyr is distributed in the gas phase,
8 the yields of 1-NP that formed in the filter were smaller than 5% and the partition ratios in the
9 gas and particulate phases of Pyr depend on temperature (Nielsen, 1983; Yamasaki et al.,
10 1982). Figure 4 shows the [1-NP]/[Pyr] ratios in the atmospheric particulates collected at the
11 two sites of Shenyang in 2001 - 2002 and 2007. During the intervening 5 years, the
12 [1-NP]/[Pyr] ratios in winter increased from 0.003 to 0.014 at SY-1 and from 0.002 to 0.010
13 at SY-2. In summer, the [1-NP]/[Pyr] ratios also increased from 0.008 (2001) to 0.025 (2007)
14 at SY-1. Although no data was obtained at SY-2 in summer 2001, the [1-NP]/[Pyr] ratio was
15 very high (0.025) as well. Furthermore, the [1-NP]/[Pyr] ratio variance at SY-1 was larger in
16 summer than in winter. The [1-NP]/[Pyr] ratio of particulates emitted by coal combustion
17 systems (0.001) was much smaller than the ratio of particulates emitted by diesel-engine
18 automobiles (0.36) (Tang et al., 2005). These results suggest that motor vehicles became one
19 of the major contributors of atmospheric PAHs and NPAHs in Shenyang in 2007 not only in
20 summer but also in winter.

21

22 **Conclusions**

23

24 The concentrations and distribution of PAHs and NPAHs in different particulate size
25 fractions changed between 2001 - 2002 and 2007. In winter, the concentrations of coarse size

1 particulates ($> 2.1 \mu\text{m}$) in the atmosphere decreased from 57.5% to 44.6% over the 5-year
2 period. Concurrently, the concentrations of atmospheric PAHs and NPAHs in winter in the
3 coarse size particulate fractions, which might have originated from inefficient boilers,
4 decreased from $0.35 \text{ pmol } \mu\text{g}^{-1}$ to $0.15 \text{ pmol } \mu\text{g}^{-1}$, and $0.55 \text{ fmol } \mu\text{g}^{-1}$ to $0.32 \text{ fmol } \mu\text{g}^{-1}$,
5 respectively, during the 5 years. Especially, the concentrations of PAHs and NPAHs in winter
6 2007 decreased significantly from the concentrations in winter 2002, probably largely as a
7 result of Shenyang's Blue Sky Project. However, both PAH and NPAH concentrations in
8 summer increased from 2001 to 2007, and the concentrations of NPAHs in winter did not
9 change markedly between 2002 and 2007. Our comparative data on the particulate
10 distributions, seasonal variations and compositions of PAHs and NPAHs in the atmosphere
11 show that motor vehicles have become one of the major contributors of atmospheric PAHs
12 and NPAHs in Shenyang not only in summer but also in winter.

13

14 **Acknowledgements**

15 This research was supported in part by a Grant in Aid for Scientific Research (Nos.
16 21256001, 21120503 and 21590132) from the Ministry of Education, Culture, Sports, Science
17 and Technology, Japan and Steel Industry Foundation for the Advancement of Environmental
18 Protection Technology. This research was also a Joint Project supported by Japan-China
19 Medical Association. The authors thank Susumu Hayakari of Aomori Prefectural Institute of
20 Public Health and Environment, Japan for providing statistical analysis software program.

21

22 **References**

23 Arey, J., Zielinska, B., Atkinson, R., Winer, A.M., Ramdahl, T. and Pitts, J.N. 1986. The
24 formation of nitro-PAH from the gas-phase reactions of fluoranthene and pyrene with the
25 OH radical in the presence of NO_x. *Atmospheric Environment* 20: 2339-2345.

- 1 Bourotte, C., Forti, M. C., Taniguchi, S., Bicego, M. C. and Lotufo, P. A. 2005. A wintertime
2 study of PAHs in fine and coarse aerosols in Sao Paulo city, Brazil. *Atmospheric*
3 *Environment* 39:3799-3811.
- 4 Hayakawa, K., Kitamura, R., Butoh, M., Imaizumi, N. and Miyazaki, M. 1991. Determination
5 of diamino- and aminopyrenes by high performance liquid chromatography with
6 chemiluminescence detection. *Analytical Sciences* 7:573-577.
- 7 Hayakawa, K., Murahashi, T., Butoh, M. and Miyazaki, M. 1995a. Determination of 1,3-, 1,6-,
8 and 1,8-dinitropyrenes and 1-nitropyrene in urban air by high-performance liquid
9 chromatography using chemiluminescence detection. *Environmental Science and*
10 *Technology* 29:928-932.
- 11 Hayakawa, K., Kawaguchi, Y., Murahashi, T. and Miyazaki, M. 1995b. Distributions of
12 nitropyrenes and mutagenicity in airborne particulates collected with an Andersen sampler.
13 *Mutation Research* 348:57-61.
- 14 Hayakawa, K., Murahashi, T., Akutsu, K., Kanda, T., Tang, N., Kakimoto, H., Toriba, A. and
15 Kizu, R. 2000. Comparison of polycyclic aromatic hydrocarbons and nitropolycyclic
16 aromatic hydrocarbons in airborne and automobile exhaust particulates. *Polycyclic*
17 *Aromatic Compounds* 20:179-190.
- 18 Hayakawa, K., Tang, N., Akutsu, K., Murahashi, T., Kakimoto, H., Kizu, R. and Toriba, A.
19 2002. Comparison of polycyclic aromatic hydrocarbons and nitropolycyclic aromatic
20 hydrocarbons in airborne particulates collected in downtown and suburban Kanazawa,
21 Japan. *Atmospheric Environment* 36:5535-5541.

- 1 Hayakawa, K., Tang, N., Kameda, T. and Toriba, A. 2007. Atmospheric behaviors of
2 polycyclic aromatic hydrocarbons and nitropolycyclic aromatic hydrocarbons in East Asia.
3 *Asian Journal of Atmospheric Environment* 1:19-27.
- 4 Hattori, T., Tang, N., Tamura, K., Hokota, A., Yang, X.Y., Igarashi, K., Ohno, M., Okada, Y.,
5 Toriba, A. and Hayakawa, K. 2007. Profiles of particulate-bound polycyclic aromatic
6 hydrocarbons and their nitrated derivatives in three typical cities, Liaoning Province, China.
7 *Environmental Forensics* 8:165-172.
- 8 Ho, K.F., Cao, J.J., Lee, S.C. and Chan, C.K. 2006. Source apportionment of PM_{2.5} in urban
9 area of Hong Kong. *Journal of Hazardous Materials* 138: 73-85.
- 10 IARC, 2005. *IARC Monographs on the Evaluation of the Carcinogenic Risks to Humans*,
11 IARC, Lyon, 92.
- 12 Kakimoto, H., Kitamura, M., Matsumoto Y., Sakai S., Kanoh, F., Murahashi, T., Akutsu K.,
13 Kizu, R. and Hayakawa, K. 2000. Comparison of atmospheric polycyclic aromatic
14 hydrocarbons and nitropolycyclic aromatic hydrocarbons in Kanazawa, Sapporo and Tokyo.
15 *Journal of Health Science* 46:5-15.
- 16 Kakimoto, H., Matsumoto, Y., Sakai, S., Kanoh, F., Arashidani, K., Tang, N., Akutsu, K.,
17 Nakajima A., Awata, Y., Toriba, A., Kizu, R. and Hayakawa, K. 2002. Comparison of
18 atmospheric polycyclic aromatic hydrocarbons and nitropolycyclic aromatic hydrocarbons
19 in an industrialized city (Kitakyushu) and two commercial cities (Sapporo and Tokyo).
20 *Journal of Health Science* 48:370-375.
- 21 Kawanaka, Y., Matsumoto, E., Sakamoto, K., Wang, N. and Yun, S.J. 2004. Size distributions
22 of mutagenic compounds and mutagenicity in atmospheric particulate matter collected with
23 a low-pressure cascade impactor. *Atmospheric Environment* 38:2125-2132.

- 1 Kizu, R., Ishii, K., Kobayashi, J., Hashimoto, T., Koh, E., Namiki, M. and Hayakawa, K.
2 2000. Antiandrogenic effect of crude extract of C-heavy oil. *Materials Science and*
3 *Engineering: C* 12:97–102.
- 4 Kong, S., Ding, X., Bai, Z., Han, B., Chen, L., Shi, J. and Li, Z. 2010. A seasonal study of
5 polycyclic aromatic hydrocarbons in PM_{2.5} and PM_{2.5-10} in five typical cities of Liaoning
6 Province, China. *Journal of Hazardous Materials* 183: 70-80.
- 7 Nielsen, T.A. 1983. The formation and presence for nitro derivatives of polycyclic aromatic
8 hydrocarbons in the atmosphere. *Proceedings of the World Congress on Air Quality* 1:
9 239-243.
- 10 Rogge, W. F., Hildemann, L.M., Mazurek, M.A., Cass, G. R. and Simoneit, B.R.T. 1993.
11 Sources of fine organic aerosol. 2. Noncatalyst and catalyst-equipped automobiles and
12 heavy-duty diesel trucks. *Environmental Science and Technology* 27:636-651.
- 13 Shenyang Environmental Protection Bureau of China (<http://www.syepb.gov.cn/>).
- 14 Tang, N., Tabata, M., Mishukov, V. F., Sergienko, V., Toriba, A., Kizu, R. and Hayakawa, K.
15 2002a. Comparison of atmospheric nitropolycyclic aromatic hydrocarbons in Vladivostok,
16 Kanazawa and Toyama. *Journal of Health Science* 48:30-35.
- 17 Tang, N., Oguri, M., Watanabe, Y., Tabata, M., Mishukov, V. F., Sergienko, V., Toriba, A.,
18 Kizu, R. and Hayakawa, K. 2002b. Comparison of atmospheric polycyclic aromatic
19 hydrocarbons in Vladivostok, Toyama and Kanazawa. *Bulletin of the Japan Sea Research*
20 *Institute, Kanazawa University* 33:77-86.
- 21 Tang, N., Toriba, A., Kizu, R. and Hayakawa, K. 2003. Improvement of an automatic HPLC
22 system for nitropolycyclic aromatic hydrocarbons: Removal of an interfering peak and
23 increase in the number of analytes. *Analytical Sciences* 19:249-253.

1 Tang, N., Hattori, T., Taga, R., Igarashi, K., Yang, X.-Y., Tamura, K., Kakimoto, K.,
2 Mishukov, V.-F., Toriba, A., Kizu, R. and Hayakawa, K. 2005. Polycyclic aromatic
3 hydrocarbons and nitropolycyclic aromatic hydrocarbons in urban air particulates and their
4 relationship to emission sources in the Pan-Japan Sea countries. *Atmospheric Environment*
5 39:5817-5826.

6 Tang, N., Araki, Y., Tamura, K., Dong, L. J., Zhang, X. M., Liu, Q. H., Ji, R. N., Kameda, T.,
7 Toriba, A. and Hayakawa, K. 2009. Distribution and source of atmospheric polycyclic
8 aromatic hydrocarbons and nitropolycyclic aromatic hydrocarbons in Tieling city, Liaoning
9 Province, a typical local city in China. *Asian Journal of Atmospheric Environment* 3:52-58.

10 Yamasaki, H., Kuwata, K., Miyamoto, H. 1982. Effect of ambient temperature on aspects of
11 airborne polycyclic aromatic hydrocarbons. *Environmental Science and Technology* 16:
12 189-194.

13
14
15
16
17
18
19
20
21
22
23
24

1 **Figure Captions**

2

3 **Figure 1.** Comparison of atmospheric PAHs and NPAHs at two sites in Shenyang in 2001 -
4 2002 and in 2007. Each bar means the average concentration of total PAHs or NPAHs; PAHs
5 includes FR, Pyr, BaA, Chr, BbF, BkF, BaP, BgPe and IDP; NPAHs includes 1-NP, 6-NC and
6 6-NBaP. The data of Shenyang in 2001 - 2002 are from Hattori et al., 2007.

7

8 **Figure 2.** Particulate partitions of PAHs, NPAHs and APs in three size fractions at two sites in
9 Shenyang in 2001 - 2002 and in 2007. Three size fractions mean larger 7 μm , 7 - 2.1 μm and
10 smaller than 2.1 μm . The data of Shenyang in 2001 - 2002 referenced from Hattori et al.,
11 2007. The concentrations of PAHs, NPAHs and APs in each particulate size fraction are
12 shown within each box.

13

14 **Figure 3.** Cluster analysis dendrogram of atmospheric PAHs and NPAHs at two sites in
15 Shenyang and in Tokyo by using Ward's method and standardized squared Euclidean distance.
16 The parameters used for the cluster analysis were the concentration ratios of 1-NP to Pyr,
17 6-NBaP to BaP and individual PAH to total PAHs in the airborne particulates collected at two
18 sites in 2001 - 2002 and 2007.

19

20 **Figure 4.** Comparison of [1-NP]/[Pyr] ratios at two sites in Shenyang. The data of Shenyang
21 in 2001 - 2002 are from Hattori et al., 2007.

22

23

24

1 Table 1 Atmospheric concentrations of nine PAHs and four NPAHs in 2007 at two sites in
 2 Shenyang, China.

		Summer		Winter	
		SY-1	SY-2	SY-1	SY-2
PAH	FR	7.97 ± 3.55	7.22 ± 3.33	67.9 ± 36.0	51.6 ± 26.7
(pmol m ⁻³)	Pyr	6.99 ± 2.60	6.41 ± 2.63	70.1 ± 34.8	60.3 ± 31.8
	BaA	7.11 ± 3.63	5.41 ± 2.94	63.1 ± 28.2	57.9 ± 35.2
	Chr	13.4 ± 7.52	9.91 ± 6.19	79.8 ± 34.3	67.5 ± 34.0
	BbF	34.3 ± 28.5	28.7 ± 27.9	69.9 ± 32.9	61.8 ± 32.4
	BkF	11.2 ± 8.66	9.71 ± 8.62	26.5 ± 11.9	24.9 ± 12.6
	BaP	11.4 ± 6.45	10.2 ± 6.70	44.1 ± 19.3	42.9 ± 22.1
	BgPe	24.6 ± 13.8	23.1 ± 14.9	46.0 ± 17.1	56.2 ± 26.5
	IDP	14.4 ± 8.57	14.6 ± 10.0	22.2 ± 9.24	27.5 ± 13.1
	Total PAHs	131 ± 80.2	115 ± 79.6	491 ± 215	451 ± 226
NPAH	9-NA	718 ± 400	600 ± 369	5400 ± 3280	5430 ± 3210
(fmol m ⁻³)	1-NP	159 ± 49.8	147 ± 54.7	857 ± 459	555 ± 184
	6-NC	205 ± 100	191 ± 86.0	544 ± 260	343 ± 157
	6-NBaP	31.9 ± 15.6	32.4 ± 14.6	116 ± 58.5	93.4 ± 64.1
	Total NPAHs	1110 ± 526	972 ± 493	6910 ± 3450	6420 ± 3410

3
 4 All data represent mean ± S.D., n = 7.

5
 6
 7
 8
 9
 10
 11
 12
 13
 14
 15
 16
 17

1 Table 2 Correlation coefficients between PAHs, NPAHs and APs in different particulate
 2 fractions and several meteorological conditions.

		Winter			Summer		
		Temperature (°C)	Wind speed (m s ⁻¹)	Humidity (%)	Temperature (°C)	Wind speed (m s ⁻¹)	Humidity (%)
Meteorological Condition	Wind speed (m s ⁻¹)	-0.58			-0.71		
	Humidity (%)	0.27	-0.81*		-0.63	0.19	
SY-1	PAHs (> 7 μm)	0.24	-0.64	0.79*	0.20	0.12	-0.83**
	PAHs (7 - 2.1 μm)	0.54	-0.74	0.82**	0.04	0.31	-0.75*
	PAHs (< 2.1 μm)	0.43	-0.81*	0.92**	-0.11	0.56	-0.63
	NPAHs (> 7 μm)	0.41	-0.47	0.37	0.18	-0.18	-0.73
	NPAHs (7 - 2.1 μm)	0.61	-0.65	0.50	0.03	-0.02	-0.67
	NPAHs (< 2.1 μm)	0.27	-0.63	0.70	0.13	0.18	-0.82**
	APs (> 7 μm)	-0.49	0.90**	-0.84**	0.04	-0.04	-0.63
	APs (7 - 2.1 μm)	-0.11	0.70	-0.58	-0.05	-0.04	-0.55
	APs (< 2.1 μm)	0.76	-0.64	0.57	-0.20	0.14	-0.49
SY-2	PAHs (> 7 μm)	0.48	-0.81*	0.83**	0.21	0.07	-0.84**
	PAHs (7 - 2.1 μm)	0.62	-0.77*	0.61	0.09	0.17	-0.76*
	PAHs (< 2.1 μm)	0.34	-0.77*	0.79*	-0.14	0.57	-0.52
	NPAHs (> 7 μm)	0.42	-0.75*	0.73	0.34	0.05	-0.88**
	NPAHs (7 - 2.1 μm)	0.66	-0.92**	0.76*	0.16	0.21	-0.79*
	NPAHs (< 2.1 μm)	0.63	-0.87**	0.79*	0.18	0.10	-0.86**
	APs (> 7 μm)	-0.39	0.90**	-0.90**	0.47	-0.21	-0.90**
	APs (7 - 2.1 μm)	-0.00	0.50	-0.62	0.18	0.01	-0.79*
	APs (< 2.1 μm)	0.68	-0.66	0.53	-0.04	0.19	-0.61

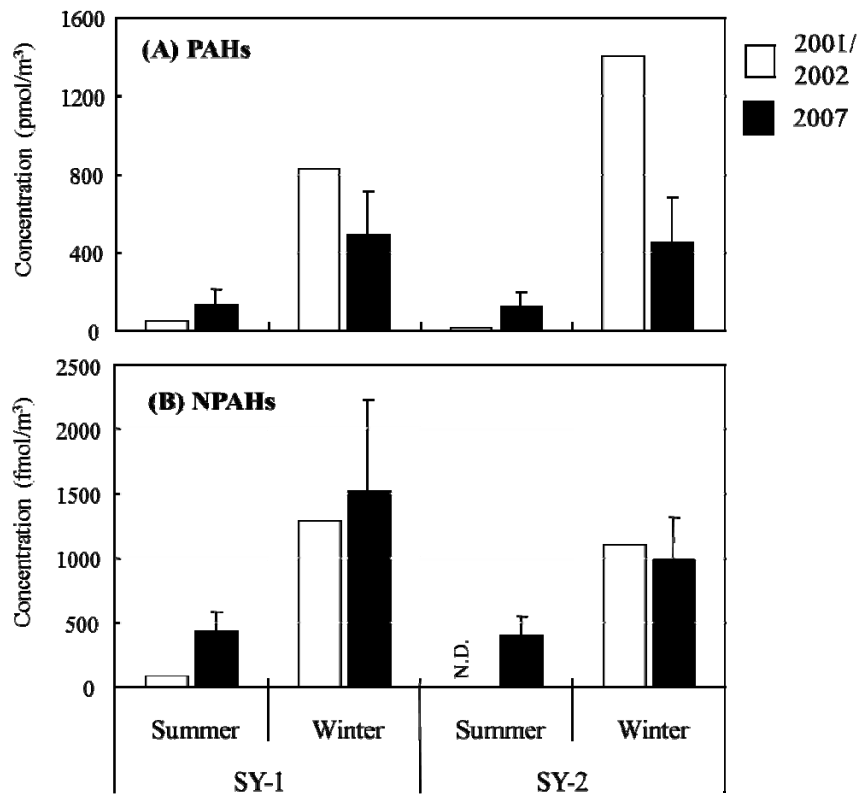
3
 4 n = 7. The data of average temperature, dew point and wind speed in Shenyang during the
 5 sampling periods were obtained from USA National Climatic Data Center
 6 (<http://lwf.ncdc.noaa.gov/oa/climate/onlineprod/drought/xmgr.html#gr>) and average humidity
 7 were calculated by using the data of average temperature and dew point.

8
 9
 10
 11
 12
 13
 14
 15
 16

1

2

Fig. 1



3

4

5

6

7

8

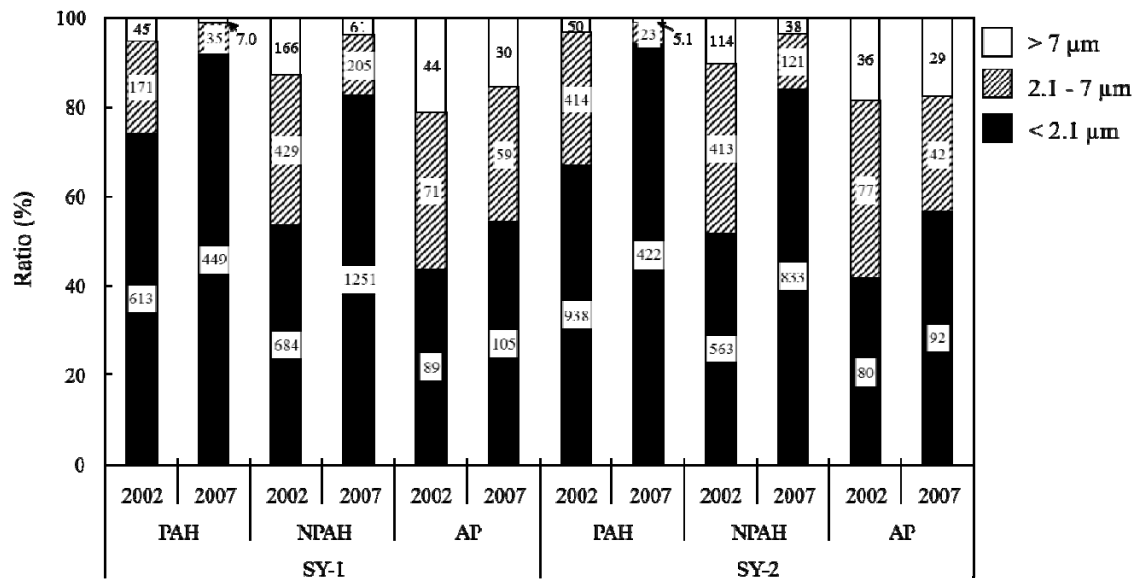
9

10

11

12

Fig. 2



1

2

3

4

5

6

7

8

9

10

11

12

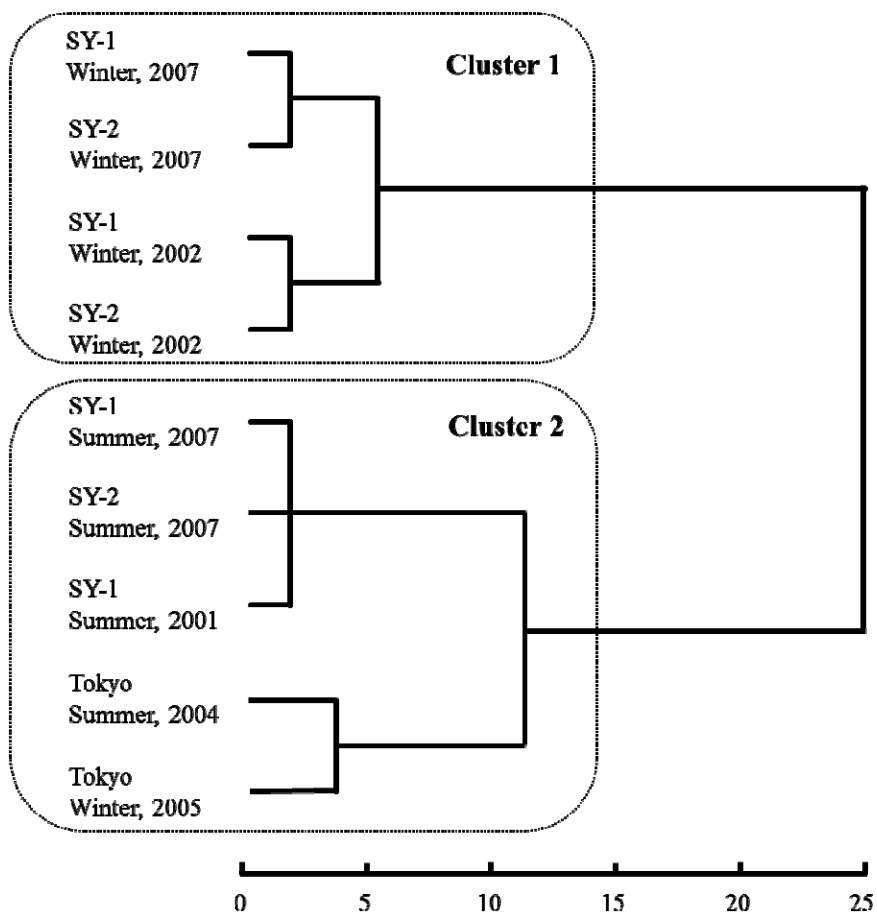
13

14

15

16

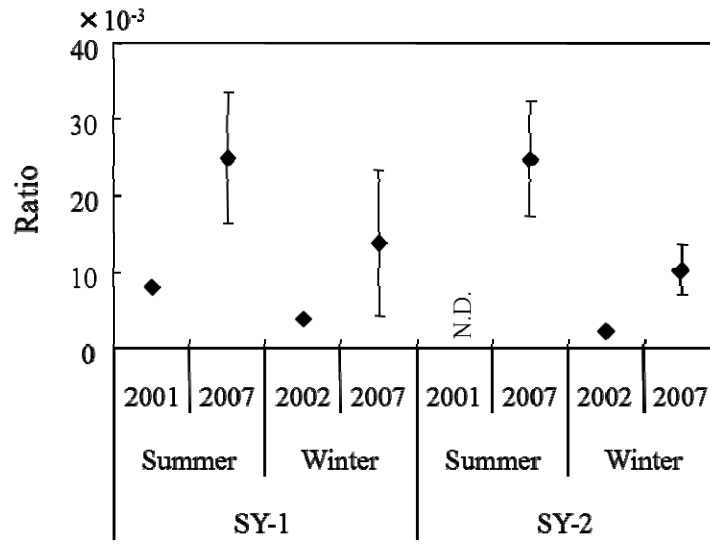
Fig. 3



1
2
3
4
5
6
7
8
9
10

1

Fig. 4



2

3