Comparison of Air Pollution in Metropolises in China (Beijing) and Japan (Osaka and Nagoya) on the Basis of the Levels of Contaminants and Mutagenicity

Souleymane Coulibaly, a Hiroki Minami, a Maho Abe, b Nami Furukawa, a Ryo Ono, a Tomohiro Hasei, a Akira Toriba, b Ning Tang, b Kazuichi Hayakawa, b Kunihiro Funasaka, c Daichi Asakawa, f Fumikazu Ikemori, d Masanari Watanabe, c Naoko Honda, a, f Keiji Wakabayashi, a, f and Tetsushi Watanabe * a

a Department of Public Health, Kyoto Pharmaceutical University; 1 Misasagi-Shichonocho, Yamashina-ku, Kyoto 607–8412, Japan; b Institute of Medical, Pharmaceutical and Health Sciences, Kanazawa University; Kakuma-machi, Kanazawa, Ishikawa 920–1192, Japan; c Osaka City Institute of Public Health and Environmental Sciences; 8–34 Toijo-ko, Tennoji-ku, Osaka 543–0026, Japan; d Nagoya City Institute for Environmental Sciences; 5–16–8 Toyoda, Minami-ku, Nagoya 457–0841, Japan; e Department of Respiratory Medicine and Rheumatology, Faculty of Medicine, Tottori University; 36–1 Nishimachi, Yonago, Tottori 683–8504, Japan; f Department of Food and Nutrition, Faculty of Human Health, Sonoda Women’s University; 7–29–1 Minamitsukaguchicho, Amagasaki, Hyogo 661–8520, Japan; and g Graduate Division of Nutritional and Environmental Sciences, University of Shizuoka; 52–1 Yada, Suruga-ku, Shizuoka 422–8526, Japan.

Received November 7, 2015; accepted November 23, 2015

Public concern regarding the transport of air pollutants from mainland East Asia to the leeward area by the prevailing westerlies in spring and winter monsoon has been growing in recent years. We collected total suspended particle (TSP) in Beijing, a metropolis of China located windward of Japan, in spring (late February 2011–May 2011) and in winter (November 2012–early February 2013), then analyzed metals, ions, and organic compounds and mutagenicity, and compared the pollution levels with samples collected at two Japanese metropolises (Osaka and Nagoya) during the same periods. The medians of concentration of TSP and other factors in Beijing were much larger than those in the Japanese metropolises. Especially, the concentrations of polycyclic aromatic hydrocarbons (PAHs) were remarkably high in Beijing in winter, and the median of total PAHs concentration in Beijing was 62–63 times larger than that in the Japanese sites. The mutagenicity of TSP from Beijing toward Salmonella typhimurium YG1024, with and without a mammalian metabolic system (S9 mix), was 13–25 times higher than that from the Japanese sites in winter. These results suggest that air pollution levels in Beijing are very high compared with those at the two Japanese metropolises we evaluated. The diagnostic ratios of PAHs and nitrated polycyclic aromatic hydrocarbons (NPAHs) suggest that the major sources of PAHs and NPAHs in Beijing are different from those at the two Japanese sites in winter, and that the major source in Beijing is coal/biomass combustion.

Key words airborne particle; Ames test; polycyclic aromatic hydrocarbon; metal; water soluble ionic species; nitrated polycyclic aromatic hydrocarbon

The International Agency for Research on Cancer (IARC) has classified outdoor air pollution and particulate matter, which is a major component of outdoor air pollution, as carcinogenic to humans (group 1). 5 In recent decades, primary energy consumption has rapidly increased in northeast Asia, especially in China, 6 and as the consequence of unprecedented economic development and industrial growth in China, the emissions of anthropogenic air pollutants have drastically increased. Coal is the primary energy source in China, 7 and the vast majority of coal has been consumed in northern, central, and eastern China. 8 The Beijing–Tianjin–Hebei region is located in northern China and is of special concern because of severe haze. 9 Haze is an atmospheric phenomenon where visibility is decreased by dry particulate matters, such as dust and smoke. Zhao et al. 10 collected PM 2.5 (airborne particles with an aerodynamic diameter of less than or equal to 2.5 µm) at four urban sites in the Beijing–Tianjin–Hebei region over four seasons from 2009 to 2010, and revealed that the PM 2.5 concentrations at Shijiazhuang and Chengde were highest in winter and that the PM 2.5 pollution was dominated by coal combustion. Various mutagenic/carcinogenic substances, such as polycyclic aromatic hydrocarbons (PAHs) and nitrated PAHs (NPAHs), are generated by the incomplete combustion of fossil fuels, such as coal and petroleum, by anthropogenic activities, and emitted into the atmosphere. 5–9

Several studies have reported that dust particles and anthropogenic air pollutants have been transported by the prevailing westerlies and winter monsoon from mainland East Asia to leeward areas, including Taiwan, Korea, and Japan. 10–12 We examined air pollutants containing mutagens and other chemicals in western Japan, namely, Dazaifu in Fukuoka Prefecture and Yurihama in Tottori Prefecture, for one year. Highly mutagenic airborne particles were collected at both sites in January and February 2013. 13,14 At Yurihama, high mutagenicity was also detected in many samples collected in March 2013. 14 Because atmospheric concentrations of lead (Pb) and sulfate ion (SO 4 2– ), which are indicators of transboundary air pollution from mainland East Asia, 15,16 were increased in those particles, the mutagens in those particles were presumed to be transported from mainland East Asia. However, information
on the air pollution containing mutagens and the mutagenicity of airborne particles in the windward side, China, is limited.

The purpose of this study was to clarify the air pollution levels at Beijing, which is a metropolitan in China and is located windward of Japan, in winter and spring, and to compare the pollution levels with those at metropolises in Japan, namely, Osaka and Nagoya. Beijing has a population density of about 5500/km² (population, 21009000; area, 3820 km²) in 2014. Osaka and Nagoya are the central cities of Kansai and Chukyo metropolitan area, respectively. The population density of Osaka was 11960/km² (population, 2694000; area, 225 km²) and that of Nagoya was 6990/km² (population, 2280000; area, 326 km²) in 2015. We collected airborne particles at those three sites in spring and winter, quantified the constituents, and examined their bacterial mutagenicity. As constituents, we analyzed iron (Fe), Pb, SO₄²⁻, nitrate ion (NO₃⁻), PAHs, and NPAHs. Fe is a major element in the earth’s crust and is an indicator of the amount of sand in total suspended particle (TSP). Pb is a minor element in the crust and is emitted into the atmosphere by combustion of coal and refuse incineration. SO₄²⁻ and NO₃⁻ are formed from sulfur oxides and nitrogen oxides, which are produced by combustion of fossil fuels, such as coal and petroleum. PAHs and NPAHs are formed by incomplete combustion of organic substances and are representative environmental mutagens/carcinogens. Mutagenicity was examined using Salmonella typhimurium YG1024, which is sensitive to atmospheric mutagens without and with a mammalian metabolic activation system (S9 mix). Moreover, we calculate diagnostic ratios of chemical constituents, namely, PAHs and NPAHs, to estimate the sources of air pollutants.

MATERIALS AND METHODS

Chemicals Pyrene (PY, CAS 129-00-0) and fluoranthene (FR, CAS 206-44-0) were purchased from Nacalai Tesque Inc. (Kyoto, Japan). 2-Acetylaminofluorene (CAS 53-96-3), benzo[a]anthracene (BaA, CAS 56-55-3), 1-nitropyrene (1-NPY, CAS 5522-43-0), 2-nitropyrene (2-NPY, CAS 789-07-1), 4-nitropyrene (4-NPY, CAS 57835-92-4), and dibenz[a,h]-anthracene (DahA, CAS 53-70-3) were obtained from Tokyo Chemical Industry Co., Ltd. (Tokyo, Japan). 2-Nitrofluoranthene (2-NFR, CAS 13177-29-2) was obtained from Chiron AS (Trondheim, Norway). Benzo[k]fluoranthene (BkF, CAS 207-08-9), indeno[1,2,3-cd]pyrene (IcdP, CAS 193-39-5), benzo[j]fluoranthene (BjF, CAS 205-99-2), benzo[a]pyrene (BaP, CAS 50-32-8), nitric acid (HNO₃, CAS 7697-37-2), perchloric acid (HClO₄, CAS 7601-90-3), and hydrochloric acid (HCl, CAS 7647-01-0) were obtained from Wako Pure Chemical Industries, Ltd. (Osaka, Japan). Phenobarbital (CAS 50-06-6), chrysene (CH, CAS 218-01-9), β-naphthoflavone (CAS 6051-87-2), benzo[ghi]perylene (BghiP, CAS 191-24-2), 3-nitrofluoranthene (3-NFR, CAS 892-21-7), and 6-nitrochrysene (6-NCH, CAS 7496-02-8) were obtained from Sigma-Aldrich Co., LLC (St. Louis, MO, U.S.A.).

Sampling TSP were collected at three sites (Fig. 1), namely, Beijing (116.34°E, 40.01°N), Osaka (135.53°E, 34.99°N), and Nagoya (136.92°E, 35.10°N). Sampling was performed by the method described previously. TSP were collected on quartz filters (Pall Life Sciences, Port Washington, NY, U.S.A.) at a flow rate of 400–1000 L/min for about 24 h using a high volume air sampler (HV1000R, Shibata Scientific Technology, Soka, Japan). Sampling was performed in spring (late February 2011–May 2011) and winter (November 2012–early February 2013) as shown in Table 1. The sampling periods were each 20 d at Beijing and 16 d at Osaka and Nagoya. The amount of TSP was calculated from the difference of weights of the filter before and after sample collection, and the atmospheric concentration of TSP was calculated by dividing the weight of TSP by the volume of the air that had passed.
through the filter.

**Quantification of Metals** Fe and Pb were measured by the method described previously. Sample solutions were prepared from 10% of each sample filter by digestion using mixtures of HNO3/HCl and HNO3/HF/HClO4 and adjustment using 0.2 M HNO3. Fe and Pb were analyzed by inductively coupled plasma-atomic emission spectrometry (IRIS 1000, Thermo Fisher Scientific, Waltham, MA, U.S.A.) and Zeeman electro-thermal atomic absorption spectrometry (Analyt 600, PerkinElmer Inc., Waltham, MA, U.S.A.), respectively.

**Quantification of Water Soluble Ionic Species** SO4^2−, and NO3− were quantitated by the method described previously. Sample solutions were prepared from 5% of each sample filter by ultra-sonication with distilled water and filtration using a DISMIC-25CS syringe filter (Advantec Co., Ltd., Tokyo, Japan). SO4^2− and NO3− were analyzed using an ion chromatograph (600E/700, Waters Co., Ltd., Milford, MA, U.S.A.) with an anion suppressor (ASRS 300, Thermo Fisher Scientific, Waltham, MA, U.S.A.), respectively.

**Quantification of PAHs and NPAHs** Ten PAHs, namely, BghiP, DahA, BaP, PY, FR, IcdP, BbF, BaA, BF, and CH, which are classified as priority pollutants by the United States Environmental Protection Agency, and six NPAHs, namely, 1-NP, 2-NP, 4-NP, 6-NC, 2-NFR, and 3-NFR, were analyzed. Sample solutions were prepared from 40% of each sample filter by ultra-sonication with methanol as described previously. The extract was evaporated to dryness, and the residue was dissolved in 50% ethanol. PAHs were analyzed by HPLC using a Wakosil-PAHs column (4.6 mm i.d. × 250 mm, Wako Pure Chemical Industries, Ltd.) and a fluorescence detector (RF-20AXs, Shimadzu Co., Kyoto, Japan). The wavelengths of excitation (Ex)/emission (Em) were as follows: 1-, 2-, and 4-aminopyrene isomers, 244 nm/438 nm; 2- and 3-aminofluoranthenes, 244 nm/528 nm; and 6-aminochrysene, 270 nm/430 nm.

**Mutagenicity Assay** The mutagenicity of organic extracts of TSP was assayed by the Ames test using *Salmonella typhimurium* YG1024 with and without S9 mix. Forty percent of each sample filter was extracted with methanol by ultrasound. The extract was evaporated to dryness, and the residue was dissolved in dimethyl sulfoxide. *S. typhimurium* YG1024, which was kindly provided by Dr. Nohmi of the National Institute of Health, is an O-acetyltransferase-overproducing derivative of *S. typhimurium* TA98 and is sensitive to the mutagenicity of the organic extracts of TSP. A mammalian metabolic system (S9 mix), was prepared with livers of male Sprague-Dawley rats (SLC Inc., Shizuoka, Japan) treated with phenobarbital and β-naphthoflavone as described previously. 1-NPY and 2-acetylaminofluorene were used as positive controls without and with S9 mix, respectively. The slope of the dose–response curve obtained with three doses and duplicate plates at each dose was adopted as the mutagenic potency. Samples were judged as positive when they induced twofold increases over the average of spontaneous revertants and showed well-behaved concentrations–response patterns.

**Statistical Analysis** Statistical analysis (calculation of correlation coefficients, Dunnett’s test, and others) was carried out with Microsoft Office Excel 2013. The differences in the diagnostic ratios of PAHs and NPAHs in TSP collected at Beijing from those at two Japanese sites were analyzed by non-repeated one-way ANOVA followed by Dunnett’s test.

### RESULTS

**Atmospheric Concentrations of TSP and the Chemical Constituents** Table 2 shows the medians, minimums, and maximums of the atmospheric concentrations of TSP and the chemical constituents, namely, Fe, Pb, SO4^2−, NO3−, PAHs, and NPAHs, in the TSP collected at Beijing, Osaka, and Nagoya in spring (late February–May 2011) and winter (November 2012–early February 2013). For PAHs and NPAHs, we analyzed 10 PAHs and 6 NPAHs to estimate the levels of PAHs and NPAHs in TSP, and total PAHs and total NPAHs present the sum of the concentrations of these 10 PAHs and 6 NPAHs, respectively. In spring, the medians of the concentrations of TSP and most chemical constituents from Osaka were similar to those from Nagoya. In addition, the concentrations of the chemical constituents from Osaka and Nagoya showed similar levels. The medians of the concentrations of TSP and the constituents from Beijing were
3–12 times larger than those from the two Japanese sites. The maximums of the concentrations of TSP and the chemical constituents from Beijing were 5–57 times larger than those from Japanese sites. Large differences were found for total PAHs, and the maximum from Beijing (405.0 ng/m³) was 41 times and 57 times larger than those from Osaka (9.8 ng/m³) and Nagoya (7.1 ng/m³), respectively.

For samples collected in winter, the medians of the concentrations of TSP and most chemical constituents from Osaka were similar to those from Nagoya. The medians of the concentrations of TSP and the constituents from Beijing were 5–63 times larger than those from the two Japanese sites. Large differences were found for total PAHs and total NPAHs. For total PAHs, the medians from Beijing (146.9 ng/m³) were 63 times and 62 times larger than those from Osaka and Nagoya, respectively. The median of total NPAHs concentration from Beijing (719.6 pg/m³) was 22 times and 26 times larger than those from Osaka and Nagoya, respectively. The maximums of the concentrations of TSP and the constituents from Beijing were 6–278 times larger than those from the Japanese sites. Large differences were found for total PAHs, and the maximum concentration from Beijing (1407.3 ng/m³) was 88 times and 278 times larger than those from Osaka and Nagoya, respectively. The maximum concentration of total NPAHs from Beijing (1657.3 pg/m³) was about 20 times larger than those from the two Japanese sites.

For Osaka and Nagoya, there was no large difference in the median for the concentrations of TSP and all chemical constituents between spring and winter. For Beijing, the medians for TSP and most chemical constituents showed similar levels in the two sampling periods. However, the medians for total PAHs and total NPAHs in winter were 8 times and 6 times larger than those in spring, respectively.

**Mutagenic Activity of TSP** Table 3 shows the medians, minimums, and maximums of the mutagenicities of organic extracts of TSP collected at Beijing, Osaka, and Nagoya in spring and winter. In spring, the medians of the mutagenicities of TSP from Osaka and Nagoya were similar under each metabolic condition, namely, the absence or the presence of S9 mix. The medians of the mutagenicities of TSP from Beijing without and with S9 mix (198.5 revertants (rev.)/m³ and 423.5 rev./m³, respectively) were 6–9 times larger than those from Osaka and Nagoya. The maximums of the mutagenicities of TSP from Beijing without and with S9 mix (2176.8 and 5214.9 rev./m³, respectively) were 15–30 times larger than those from Osaka and Nagoya, respectively. In winter, there were no large differences between the mutagenicities of TSP from Osaka and Nagoya without or with S9 mix. The medians of the mutagen-
Correlations between Mutagenicity and Atmospheric Concentrations of TSP and the Constituents

To clarify the association between the mutagenicity and the levels of contaminants, we calculated their coefficients of correlation. Table 4 summarizes the correlation coefficients ($r$) between the mutagenicity and the atmospheric concentrations of TSP and the constituents in TSP collected at Beijing, Osaka, and Nagoya for the two periods. At Beijing, strong ($r \geq 0.7$) or moderate ($0.7 > r \geq 0.4$) positive correlations were obtained for TSP and most constituents without and with S9 mix in spring and winter. The correlations between the mutagenicity with and without S9 mix and the concentrations of Pb, $\text{SO}_4^{2-}$, and total PAHs were very strong ($r \geq 0.9$) in spring. At Osaka and Nagoya, strong or moderate positive correlations were found between the mutagenicity and the concentrations of total PAHs and total NPAHs in spring and winter both without and with S9 mix.

Diagnostic Ratios of PAHs and NPAHs

To characterize the emission sources of PAHs and NPAHs, we calculated diagnostic ratios of PAHs and NPAHs in TSP collected at Beijing, Osaka, and Nagoya in spring and winter. Figure 2 shows the ratio of the concentration of IcdP to that of IcdP and BghiP ($[\text{IcdP}] / ([\text{IcdP}] + [\text{BghiP}])$) for TSP collected at each site in the two seasons. In spring, the $[\text{IcdP}] / ([\text{IcdP}] + [\text{BghiP}])$ ratio for TSP from Beijing were not significantly different from those for TSP from Osaka and Nagoya, and the medians

Table 3. Medians, Minimums and Maximums of the Mutagenicities of Organic Extracts from TSP

Table 4. Correlation Coefficients between the Mutagenicity and the Atmospheric Concentrations of TSP and the Constituents

Sampling periods were as follows: spring (late February 2011–May 2011) and winter (November 2012–early February 2013). Sampling periods were each 20 d at Beijing and 16 d at Osaka and Nagoya.

Correlations between Mutagenicity and Atmospheric Concentrations of TSP and the Constituents

To clarify the association between the mutagenicity and the levels of contaminants, we calculated their coefficients of correlation. Table 4 summarizes the correlation coefficients ($r$) between the mutagenicity and the atmospheric concentrations of TSP and the constituents in TSP collected at Beijing, Osaka, and Nagoya for the two periods. At Beijing, strong ($r \geq 0.7$) or moderate ($0.7 > r \geq 0.4$) positive correlations were obtained for TSP and most constituents without and with S9 mix in spring and winter. The correlations between the mutagenicity with and without S9 mix and the concentrations of Pb, $\text{SO}_4^{2-}$, and total PAHs were very strong ($r \geq 0.9$) in spring. At Osaka and Nagoya, strong or moderate positive correlations were found between the mutagenicity and the concentrations of total PAHs and total NPAHs in spring and winter both without and with S9 mix.

Diagnostic Ratios of PAHs and NPAHs

To characterize the emission sources of PAHs and NPAHs, we calculated diagnostic ratios of PAHs and NPAHs in TSP collected at Beijing, Osaka, and Nagoya in spring and winter. Figure 2 shows the ratio of the concentration of IcdP to that of IcdP and BghiP ($[\text{IcdP}] / ([\text{IcdP}] + [\text{BghiP}])$) for TSP collected at each site in the two seasons. In spring, the $[\text{IcdP}] / ([\text{IcdP}] + [\text{BghiP}])$ ratio for TSP from Beijing were not significantly different from those for TSP from Osaka and Nagoya, and the medians
of the ratios for TSP from these three sites were 0.373–0.407. In contrast, the ratio for TSP collected at Beijing in winter was significantly (p < 0.01) larger than those from the two Japanese sites. The medians of the ratio for TSP from Beijing, Osaka, and Nagoya were 0.810, 0.370, and 0.388, respectively. No large differences were found for the medians of the ratios for TSP from the two Japanese sites in the two periods. Figure 3 shows the ratio of the concentration of 1-NPY to that of PY ([1-NPY]/[PY]) for TSP collected at Beijing, Osaka, and Nagoya in the two periods. In spring, there were no significant differences between the ratio for TSP from Beijing and those from two Japanese sites. The medians of the ratios for the three sites in spring were as follows: Beijing, 0.007; Osaka, 0.011; Nagoya, 0.015. In contrast, the ratio for Beijing was significantly (p < 0.01) smaller than those for Osaka and Nagoya in winter. The medians of the ratios for TSP from Beijing, Osaka, and Nagoya were 0.004, 0.013, and 0.014, respectively.

These two diagnostic ratios suggest that the major sources of PAHs and NPAHs in TSP collected at Beijing were different from those at Osaka and Nagoya in winter.

**DISCUSSION**

To reveal and compare the air pollution levels at metropolises in China (Beijing) and Japan (Osaka and Nagoya), we collected TSP at these three sites in spring (late February 2011–May 2011) and winter (November 2012–early February 2013), quantified the constituents, and examined mutagenicity. Moreover, we calculated the diagnostic ratios of PAHs and NPAHs to estimate the sources of PAHs and NPAHs. Several ratios have been used to estimate the sources of PAHs and NPAHs in literatures. For instance, the [IcdP]/([IcdP]+[BghiP]) ratio is larger than 0.50 for PAHs emitted from coal or biomass combustion and lower than 0.50 for PAHs emitted from petroleum combustion. Zhou et al. investigated 17 PAHs in aerosol particles in urban and suburban sites of Beijing in 2003, and concluded that coal combustion for domestic heating was probably the major contributor to the higher PAHs loading in winter on the basis of the ratio of [IcdP]/([IcdP]+[BghiP]). Although the [IcdP]/([IcdP]+[BghiP]) ratio is one of the most commonly used ratios to estimate the source of PAHs in airborne particles, the
differences of the ratios among PAHs sources are not large enough to identify the source in some cases. Therefore, we adopted another diagnostic ratio, namely, [1-NPY]/[PY], to estimate the source of PAHs and NPAHs. The [1-NPY]/[PY] ratio for coal-smoke particulates (0.001) was much smaller than the ratio of diesel-engine exhaust particles (0.36).20 At Osaka and Nagoya, the medians of the concentrations of TSP and the chemical constituents were similar in the two periods. At Beijing, the medians of the concentrations of TSP, Fe, Pb, SO$_2^-$, and NO$_x$ were also similar in the two periods, but they were 3–14 times larger than those for the two Japanese sites (Table 2). On the other hand, the medians for total PAHs and total NPAHs in TSP collected at Beijing in winter were 6–8 times larger than those in spring, and the medians for PAHs and NPAHs from Beijing in winter were 62–63 and 22–26 times larger than those from the two Japanese sites. These pollution levels were similar to those reported in the previous study.28 These results indicate that air pollution with PAHs and NPAHs was very severe at Beijing in winter as compared with the two Japanese metropolises. The high values of the [IcdP]/(IcdP)+(BghiP)] ratio for TSP from Beijing in winter (median, 0.810, Fig. 2) suggest the dominance of coal combustion emissions such as domestic heating. The small ratio of [1-NPY]/[PY] for Beijing in winter (median, 0.004, Fig. 3) also implies a large effect of coal combustion on the atmospheric PAHs. The medians for total PAHs and total NPAHs from the two Japanese sites were similar in the two periods and the [IcdP]/(IcdP)+(BghiP)] and [1-NPY]/[PY] ratios for the two Japanese sites were significantly different from those for Beijing in winter. These results suggest that the effects of long-range transport of air pollution from Beijing were not large in Osaka and Nagoya in winter.

At each sampling site, the medians of the mutagenicities of TSP with and without S9 mix were larger in winter than in spring (Table 3). The medians of the mutagenicities of TSP from Beijing were 6–9 times larger than those from Osaka and Nagoya in spring, and the medians of the mutagenicities for Beijing were 13–25 times larger than those from the two Japanese sites in winter. At Beijing, strong or moderate positive correlations with the mutagenicity were observed for TSP and most constituents without and with S9 mix in spring and winter (Table 4). At Osaka and Nagoya, strong or moderate positive correlations were found between the mutagenicity and the concentrations of total PAHs and total NPAHs without and with S9 mix in the two periods. Pb, SO$_2^-$, NO$_x$, PAHs, and NPAHs are emitted into the atmosphere by combustion of fossil fuels. These results suggest that the atmosphere was more polluted with mutagens at Beijing as compared with the two Japanese sites, especially in winter, and the dominant mutagens at these three sites were formed by combustion. Because many kinds of PAHs and NPAHs are mutagenic toward S. typhimurium YG1024 with and without S9 mix, respectively, these chemicals may have contributed to the mutagenicity of the extract from TSP examined in the present study. Dong et al.29 detected six mutagenic/carcinogenic heterocyclic aromatic amines, such as 2-amino-1-methyl-6-phenyl-imidazo[4,5-b]-pyridine (PhIP), in airborne particles collected at urban sites in Beijing from March 2005 to January 2006, and speculated that combustion aerosols emitted from cooking, coal, and petroleum were the source of these chemicals in the atmosphere. Because these heterocyclic aromatic amines are formed by combustion of organic matter and show potent mutagenicity toward S. typhimurium YG1024 with S9 mix, these chemicals may have been present in the samples collected in the present study and have affected the mutagenicity in some extent.

The results of the present study indicate that air pollution levels were very high in Beijing, a windward area of Japan, in winter and spring as compared with those at metropolises in Japan (Osaka and Nagoya), and contamination with PAHs was quite severe in Beijing in winter. These results suggest that transboundary air pollution can occur in East Asia by winter monsoon and the prevailing westerlies. However, the diagnostic ratios of PAHs and NPAHs suggest that the effect of the long-range transport of PAHs and NPAHs from Beijing was not large at Osaka and Nagoya in winter. In our previous study of air pollution at Dazaifu and Yurihama, increases of air pollutants and mutagenicity, which were expected to occur by transboundary air pollution, were found in winter and spring.13,14 These results suggest that air pollution from domestic sources was dominant at Osaka and Nagoya, while effects of long-range transport of air pollutants were relatively small. Information on the long-range transport of air pollutants and their health effects are still limited. Further studies in this field are ongoing in our laboratory.

Acknowledgments This study was supported by the Environment Research and Technology Development Fund (C-1154) of the Japanese Ministry of the Environment and Health and Labour Sciences Research Grants for Research on Global Health Issues from the Ministry of Health, Labour, and Welfare of Japan. SC was granted scholarship assistance by Otsuka Toshimi Scholarship Foundation.

Conflict of Interest The authors declare no conflict of interest.

REFERENCES

1) International Agency for Research on Cancer. “IARC Monographs No.109.” http://monographs.iarc.fr/ENG/Publications/GeneralPrinciples.pdf
2) “BP Statistical review of world energy. June 2015.” https://www.bp.com/content/dam/bp/pdf/Energy-economics/statistical-review-2015/bp-statistical-review-of-world-energy-2015-full-report.pdf
3) Department of Energy Statistics. National Bureau of Statistics of China 2011. China energy statistical yearbook 2011. China statistics press, Beijing (2011).
4) Zhao P, Zhang X, Xu X, Zhao X. Long-term visibility trends and characteristic in the region of Beijing, Tianjin, and Hebei, China. Atmos. Res., 101, 711–718 (2011).
5) Zhao PS, Dong F, He D, Zhao XJ, Zhang WL, Yao Q, Liu HY. Characteristics of concentrations and chemical compositions for PM$_{2.5}$ in the region of Beijing, Tianjin, and Hebei, China. Atmos. Chem. Phys., 13, 4631–4644 (2013).
6) Ravindra K, Sokhi R, Grieken RV. Atmospheric polycyclic aromatic hydrocarbons: Source attribution, emission factors and regulation. Atmos. Environ., 42, 2895–2921 (2008).
7) Rogge WF, Hildemann LM, Mazurek MA, Cass GR, Simoneit BRT. Sources of fine organic aerosol. 2. Non-catalyst and catalyst-equipped automobiles and heavy-duty diesel trucks. Environ. Sci. Technol., 27, 636–651 (1993).
8) Hayakawa K, Murahashi T, Butoh M, Miyazaki M. Determination of 1,3-, 1,6-, and 1,8-dinitropyrenes and 1-nitropyrene in urban air
by high-performance liquid chromatography using chemiluminescence detection. Environ. Sci. Technol., 29, 928–932 (1995).

9) Hayakawa K, Noji K, Tang N, Toriba A, Kizu R, Sakai S, Matsumoto Y. A high-performance liquid chromatographic system equipped with online reducer, clean-up, and concentrator columns for determination of trace levels of nitropolycyclic aromatic hydrocarbons in airborne particulates. Anal. Chim. Acta, 445, 205–212 (2001).

10) Lin CY, Wang Z, Chen WN, Chang SY, Chou CCK, Sugimoto N, Zhao X. Long-range transport of Asian dust and air pollutants to Taiwan: Observed evidence and model simulation. Atmos. Chem. Phys., 7, 423–434 (2007).

11) Kim HS, Chung YS, Choi HJ. On air pollutant variations in the cases of long-range transport of dust particles observed in central Korea in the leeside of China in 2010. Air Qual. Atmos. Health, 7, 309–323 (2014).

12) Sato K, Takami A, Irie S, Miyoshi T, Ogawa Y, Yoshino A, Nakayama H, Maeda M, Hayakawa S, Hara K, Hayashi M, Kaneyasu N. Transported and local organic aerosol over Fukuoka, Japan. Aerosol. Air Qual. Res., 13, 1263–1272 (2013).

13) Coulibaly S, Minami H, Abe M, Hasei T, Sera N, Yamamoto S, Funasaka K, Asakawa D, Watanabe M, Honda N, Wakabayashi K, Watanabe T. Seasonal fluctuations of air pollution in Dazaifu, Japan, and the effect of long-range transport from mainland East Asia. Biol. Pharm. Bull., 38, 1395–1403 (2015).

14) Coulibaly S, Minami H, Abe M, Hasei T, Öro T, Funasaka K, Asakawa D, Watanabe M, Honda N, Wakabayashi K, Watanabe T. Long-range transport of mutagens and other air pollutants from mainland East Asia to western Japan. Genes Environ., 37, 25 (2015).

15) Hioki T, Nakanishi S, Mukai H, Murano K. Analysis of long-range transport of aerosols, with water-soluble ionic species and trace metal components, collected continuously with particle size segregation in the coastal area of the Sea of Japan-focusing on the Kosa event in spring 2002. J. Aerosol. Res, 21, 160–175 (2006).

16) Tsuij A, Hioki T. Detailed analysis of transboundary transport of Kosa and anthropogenic substances by size-segregated and highly time-resolved observation of ionic components and inorganic elements in ambient aerosols. J. Jpn. Soc. Atmos. Environ., 48, 82–91 (2013).

17) Mukai H, Tanaka A, Fujii T, Zeng Y, Hong Y, Tang J, Guo S, Xue H, Sun Z, Zhou J, Xue D, Zhao J, Zhai G, Gu J, Zhai P. Regional characteristics of sulfur and lead isotope ratios in the atmosphere at several Chinese urban sites. Environ. Sci. Technol., 35, 1064–1071 (2001).

18) Watanabe T, Hasei T, Kokunai O, Coulibaly S, Nishimura S, Fukasawa M, Takahashi R, Mori Y, Fujita K, Yoshihara Y, Miyake Y, Kishi A, Matsui M, Ikemori F, Funasaka K, Toriba A, Hayakawa K, Arashidani K, Inaba Y, Sera N, Deguchi Y, Seiyama T, Yamaguchi T, Watanabe M, Honda N, Wakabayashi K, Totsuka Y. Air pollution with particulate matter and mutagens: Relevance of Asian dust to mutagenicity of airborne particles in Japan. Genes Environ., 36, 120–136 (2014).

19) Hasei T, Sakaguchi M, Yoned M, Wada M, Miyagawa S, Kobayashi K, Fukuda T, Arita S, Ikemori F, Watanabe T. Development of an analytical method for strong mutagens/carcinogens, 3,9-dinitrofluoranthene and dinitropyrene isomers, in the environment and their particle-size distribution in airborne particles. Chromatographia, 78, 55–63 (2015).

20) Hasei T, Nakanishi H, Toda Y, Watanabe T. Development of two-dimensional high-performance liquid chromatography system coupled with online reduction as a new efficient analytical method of 3-nitrobenzanthrone, a potential human carcinogen. J. Chromatogr. A, 1253, 52–57 (2012).

21) Garcia-Alonso S, Barrado-Olmedo AI, Pérez-Pastor RM. An analytical method to determine selected nitro-PAHs in soil samples by HPLC with fluorescence detection. Polycyclic Aromatic Compounds, 32, 669–682 (2012).

22) Watanabe M, Ishidate M Jr, Nohmi T. Sensitive method for detection of mutagenic nitroarenes and aromatic amines: New derivatives of Salmonella typhimurium tester strains possessing elevated O-acetyltransferase levels. Mutat. Res., 234, 339–348 (1990).

23) Maron DM, Ames BN. Revised methods for the Salmonella mutagenicity test. Mutat. Res., 113, 173–215 (1983).

24) Liu S, Tao S, Liu W, Liu Y, Dou H, Zhao J, Wang L, Wang J, Tian Z, Gao Y. Atmospheric polycyclic aromatic hydrocarbons in northern China: a winter-time study. Environ. Sci. Technol., 41, 8256–8261 (2007).

25) Younger MB, Macdonald RW, Vingarzan R, Mitchell RH, Goyette D, Sylvester S. PAHs in the Fraser River Basin: a critical appraisal of PAH ratios as indicators of PAH source and composition. Org. Geochem., 33, 489–515 (2002).

26) Tang N, Hattori T, Taga R, Igarashi K, Yang XY, Tamura K, Kakinoto H, Mishukov VF, Toriba A, Kizu R, Hayakawa K. Polycyclic aromatic hydrocarbons and nitropolycyclic aromatic hydrocarbons in urban air particulates and their relationship to emission sources in the Pan-Japan Sea countries. Atmos. Environ., 39, 5817–5826 (2005).

27) Zhou J, Wang T, Huang Y, Mao T, Zhong N. Size distribution of polycyclic aromatic hydrocarbons in urban and suburban sites of Beijing, China. Chemosphere, 61, 792–799 (2005).

28) Hayakawa K, Tang N, Kameda T, Toriba A. Atmospheric behaviors of polycyclic aromatic hydrocarbons in East Asia. Genes Environ., 36, 152–159 (2014).

29) Dong X, Liu D, Gao S. Seasonal variations of atmospheric heterocyclic aromatic amines in Beijing, China. Atmos. Res., 120–121, 287–297 (2013).