Yearly variation in characteristics and health risk of polycyclic aromatic hydrocarbons and nitro-PAHs in urban Shanghai from 2010–2018

Lu Yang, Xuan Zhang, Wanli Xing, Quanyu Zhou, Lulu Zhang, Qing Wu, Zhijun Zhou, Renjie Chen, Akira Toriba, Kazuichi Hayakawa, Ning Tang

1 Graduate School of Medical Sciences, Kanazawa University, Kakuma-machi, Kanazawa, 920-1192, Japan
2 School of Public Health, Fudan University, Shanghai 200032, China
3 Institute of Medical, Pharmaceutical and Health Sciences, Kanazawa University, Kakuma-machi, Kanazawa, 920-1192, Japan
4 Institute of Nature and Environmental Technology, Kanazawa University, Kakuma-machi, 920-1192, Kanazawa, Japan

ABSTRACT

This study encompassed the regular observation of nine polycyclic aromatic hydrocarbons (PAHs) and three nitro-PAHs (NPAHs) in particulate matter (PM) in Shanghai in summer and winter from 2010 to 2018. The results showed that the mean concentrations of \( \Sigma \)PAHs in summer decreased by 24.7% in 2013 and 18.1% in 2017 but increased by 10.2% in 2015 compared to the data in 2010. However, the mean concentrations of \( \Sigma \)PAHs in winter decreased by 39.7% from 2010 (12.8 ± 4.55 ng/m\(^3\)) to 2018 (7.72 ± 3.33 ng/m\(^3\)), and the mean concentrations of 1-nitropyrene in winter decreased by 79.0% from 2010 (42.3 ± 16.1 pg/m\(^3\)) to 2018 (8.90 ± 2.09 pg/m\(^3\)). Correlation analysis with meteorological conditions revealed that the PAH and NPAH concentrations were both influenced by ambient temperature. The diagnostic ratios of PAHs and factor analysis showed that they were mainly affected by traffic emissions with some coal and/or biomass combustion. The ratio of 2-nitrofluoranthene to 2-nitropyrene was near 10, which indicated that the OH radical-initiated reaction was the main pathway leading to their secondary formation. Moreover, backward trajectories revealed different air mass routes in each sampling period, indicating a high possibility of source effects from the northern area in winter in addition to local and surrounding influences. Meanwhile, the mean total benz[a]pyrene-equivalent concentrations in Shanghai in winter decreased by 50.8% from 2010 (1860 ± 645 pg/m\(^3\)) to 2018 (916 ± 363 pg/m\(^3\)). These results indicated the positive effects of the various policies and regulations issued by Chinese authorities.

© 2020 The Research Center for Eco-Environmental Sciences, Chinese Academy of Sciences. Published by Elsevier B.V.

Introduction

Atmospheric particulate matter (PM) plays a major role in air pollution. PM can not only change the climate at the global and re-
1. Materials and methods

1.1. PM sampling

As shown in Fig. 1, PM sampling was performed in the School of Public Health, Fudan University (31.2°N, 121.4°E), located in Xuhui District, which is the central area in Shanghai, China. The sampling site was approximately 500 m away from the main road. The PM sampler was set up on the rooftop of a five-floor building.

The PM samples with aerodynamic diameters $\leq 2.1 \mu \text{m}$ (PM$_{2.1}$) and $\leq 2.1 \mu \text{m}$ (PM$_{2.1}$) were separately collected by a low-volume air sampler (AN-200, Sibata Scientific Technology Ltd., Japan) loaded onto quartz fibre filters (2500QAT-UP, Pall Co., USA). The flow rate was 28.3 L/min. PM samples were collected in summer (Aug. 8 to 20, 2013 (n = 5), Jun. 1 to 18, 2015 (n = 6) and Jul. 8 to 22, 2017 (n = 7)) and winter (Dec. 13 to 27, 2013 (n = 6), Dec.

Table 1 – Information on each individual PAH and NPAH.

<table>
<thead>
<tr>
<th>Species</th>
<th>Abbreviation</th>
<th>Ring number</th>
<th>MW*</th>
<th>TEF b</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fluoranthene</td>
<td>FR</td>
<td>4</td>
<td>202.3</td>
<td>0.001</td>
</tr>
<tr>
<td>Pyrene</td>
<td>Prr</td>
<td>4</td>
<td>202.3</td>
<td>0.001</td>
</tr>
<tr>
<td>Benzo[a]anthracene</td>
<td>BaA</td>
<td>4</td>
<td>228.3</td>
<td>0.1</td>
</tr>
<tr>
<td>Chrysene</td>
<td>Chr</td>
<td>4</td>
<td>228.3</td>
<td>0.01</td>
</tr>
<tr>
<td>Benzo[k]fluoranthene</td>
<td>BbF</td>
<td>5</td>
<td>252.3</td>
<td>0.1</td>
</tr>
<tr>
<td>Benzo[k]fluoranthene</td>
<td>BbF</td>
<td>5</td>
<td>252.3</td>
<td>0.1</td>
</tr>
<tr>
<td>Benzo[a]pyrene</td>
<td>BaP</td>
<td>5</td>
<td>252.3</td>
<td>1</td>
</tr>
<tr>
<td>Benzo[ghi]perylene</td>
<td>BgPe</td>
<td>6</td>
<td>276.3</td>
<td>0.01</td>
</tr>
<tr>
<td>Indeno[1,2,3-cd]pyrene</td>
<td>IDP</td>
<td>6</td>
<td>276.3</td>
<td>0.1</td>
</tr>
<tr>
<td>1-Nitropyrene</td>
<td>1-NP</td>
<td>4</td>
<td>247.3</td>
<td>0.1</td>
</tr>
<tr>
<td>2-Nitropyrene</td>
<td>2-NP</td>
<td>4</td>
<td>247.3</td>
<td>0.1</td>
</tr>
<tr>
<td>2-Nitrofluoranthene</td>
<td>2-NFR</td>
<td>4</td>
<td>247.3</td>
<td>0.05</td>
</tr>
</tbody>
</table>

a MW means molecular weight (g/mol).  
b TEF, means toxic equivalent factor. The values of nine PAHs are from Nisbet and Lagoy, 1992; 1-NP from OEHHA, 2005; 2-NR from Durant et al., 1996.  
<sup>c</sup> No TEF value.

1.2. Experimental analysis of the PAHs and NPAHs

The pretreatment of filters is similar to that in a previous study (Xing et al., 2020). Briefly, the PM filters (PM$_{2.1}$ and PM$_{2.1}$) were cut into several pieces. Pyrene-d$_12$ (Pyr-d$_{12}$, 98%, Wako Pure Chemicals, Osaka, Japan) and benzo[a]pyrene-d$_{12}$ (BaP-d$_{12}$, 98%, Wako Pure Chemicals, Osaka, Japan) were added to the samples as internal standards before extraction. After ultrasonic extraction, the solutions were filtered, and the extracts were successively washed with a dilute NaOH (97%, Wako Pure Chemicals, Osaka, Japan) solution (5%, W/V), H$_2$SO$_4$ (98%, Wako Pure Chemicals, Osaka, Japan) solution (20%, W/V), and distilled water. Then, the solutions were concentrated and filtered into vials. After pretreatment, nine PAHs and three NPAHs (Table 1) in each PM sample were detected by a high-performance liquid chromatography (HPLC, LC-20AD, Shimadzu Inc., Kyoto, Japan) system. The detailed detection method is shown in the Supplementary Material (Appendix A Text S1) (Tang et al., 2011).

In this study, the US EPA 610 PAH mix standard (99%) was procured from Supelco Park (Bellefonte, PA, USA), 1-NP (98%) and 2-NP (98%) were purchased from Aldrich Chemical Company (Osaka, Japan), and 2-NF (99%) was acquired from Chiron AS (Trondheim, Norway). All other reagents (analytical reagent grade) used in HPLC analysis were purchased from Wako Pure Chemicals (Osaka, Japan).

1.3. Quality control and quality assurance

To measure the background contamination during transportation, blank filters were also analysed. No target chemicals were determined, indicating that no contamination occurred during transport. The calibration curves of nine PAHs and three NPAHs all showed good linearity ($r > 0.998$), and the relative standard deviations ($n = 3$) of nine PAHs and three NPAHs were within 5%. Internal standards were used to quantify the PAHs and NPAHs. The recoveries of internal standards in all samples ranged from 80% to 103% in this study. The limit of determination and the range of calibration curves of each PAH and NPAH are shown in Appendix A Table S1.
1.4. **Data analysis**

1.4.1. **Meteorological conditions**
Meteorological conditions including average ambient temperature, relative humidity, precipitation, and average wind speed during the sampling periods were obtained from the NNDC Climate Data Online (https://www7.ncdc.noaa.gov/CDO/cdo). Appendix A Table S3 summarizes the mean value and standard deviation of meteorological conditions.

1.4.2. **Backward trajectory analysis**
The air masses during the sampling period were analysed based on the backward trajectory method with the U.S. National Oceanic and Atmospheric Association’s HYSPLIT4 model (WINDOWS-based). In this study, backward trajectories were calculated every hour, and the duration time was 24 hr (marked every 6 hr) at a sampling point height of 500 m above ground level; this height has been found to have the largest influence on the PM in Shanghai (Liu et al., 2018; Zhang et al., 2019b). All backward trajectories were classified into 3 or 4 clusters according to their characteristics of the spatial trajectory distribution during each sampling period.

1.4.3. **Health risk assessment**
The potential health risk of PAHs is often expressed by the BaP-equivalent concentration (BaPeq) (Eq. (1)) and the inhalation lifetime cancer risk (ILCR) (Eq. (2)):

\[
\text{BaPeq} = \sum (C_i \times \text{TEF}_i)
\]

\[
\text{ILCR} = \text{UR}_{\text{BaP}} \times \text{BaPeq}
\]

where, \(C_i\) (pg/m³) is each individual PAH and NPAH concentration, and \(\text{TEF}_i\) is the toxic equivalent factor of each individual PAH, 1-NP, and 2-NFR (Table 1) relative to BaP (Durant et al., 1996; Nisbet and Lagoy, 1992; OEHHA, 2005). \(\text{UR}_{\text{BaP}}\) is the unit cancer risk from BaP; as the value of \(8.7 \times 10^{-6}\) per ng/m³ used in this study was determined by the WHO in an epidemiological study of coke-oven workers (WHO World Health Organization, 2000).

1.4.4. **Statistical analysis**
IMB SPSS version 25.0 was used for statistical analysis of the data. In this study, the K-S (Kolmogorov-Smirnov) test showed that the concentrations of \(\Sigma\)PAHs and \(\Sigma\)NPAHs in summer and winter from 2013 to 2018 were normally distributed. The correlations of PAHs, NPAHs and meteorological conditions were determined by Pearson correlation analysis. A \(p\) value less than 0.05 indicated that the results were significant. Principal component analysis (PCA) can reveal high loadings of certain variables on a given factor, thereby simply and clearly identifying the various emission sources of PAHs (Ravindra et al., 2006).

2. **Results and discussion**

2.1. **Concentrations and compositions of the PM-bound PAHs and NPAHs**
The mean PAH and NPAH concentrations in PM\(_{2.5}\) from 2010 to 2018 are listed in Table 2. The \(\Sigma\)PAHs and \(\Sigma\)NPAHs concentrations in PM\(_{2.5}\) accounted for 71% to 87% of the total concentrations (PM\(_{2.5}\) + PM\(_{10}\)), Appendix A Table S2), indicating higher levels of PM-bound PAHs and NPAHs in fine particles. Because fine particles more easily penetrate the respiratory system, causing various diseases in humans (Dunea et al., 2016), this paper mainly focused on the analysis of PAHs and NPAHs in PM\(_{2.5}\).

Table 2 indicates that the mean concentrations of \(\Sigma\)PAHs in PM\(_{2.5}\) in summer did not change substantially and were relatively high in 2015 (1.83 ± 1.11 ng/m³) and low in 2013 (1.25 ± 0.51 ng/m³). In winter, compared to the data obtained in 2010 (12.8 ± 4.55 ng/m³) (Tang et al., 2013), the mean concentrations of \(\Sigma\)PAHs slightly increased in 2013 (14.2 ± 8.44 ng/m³) and then decreased in 2015 (9.51 ± 4.18 ng/m³) and 2018 (7.72 ± 3.33 ng/m³) (Table 2). The nine \(\Sigma\)PAHs concentration levels in summer and winter were both matched with the results reported by Liu et al. (2017) in Shanghai in 2014 (2.46 ng/m³ in summer and 11.6 ng/m³ in winter). These concentrations were comparable to those in Nanjing in 2013/2014 (2.99 ng/m³ in summer and 13.2 ng/m³ in winter) (Kong et al., 2018) but much lower than those in other central and northern cities, such as Wuhan in 2014 (10.34 ng/m³ in summer and 40.6 ng/m³ in winter) (Zhang et al., 2019c), Jinan in 2016 (7.55 ng/m³ in summer and 56.2 ng/m³ in winter) (Zhang et al., 2019d), Beijing in 2015 (7.81 ng/m³ in summer and 214 ng/m³ in winter) (Zhang et al., 2020b), and Shenyang from 2012 to 2014 (19.7 ng/m³ in summer and 153 ng/m³ in winter) (Yang et al., 2019). Based on the data contained in Table 2, the proportions of 4-, 5- and 6-ring PAHs (Table 1) in summer in each year each accounted for approximately one-third of \(\Sigma\)PAHs, while in winter, the order changed slightly to 4-ring > 5-ring > 6-ring PAHs. The dominant PAHs in PM\(_{2.5}\) were mostly BbF, BgPe, and IDP in summer and mostly Fr, BbF, and BgPe in winter (Table 2). These results suggest that the differences in \(\Sigma\)PAHs concentrations may be related to meteorological conditions and emission sources, which will be discussed in detail in Sections 2.2 and 2.3.

Regarding the NPAHs, in summer, Table 2 reveals that compared with 2010 (Tang et al., 2013), the mean concentrations of
1-NP in 2013 (3.49 ± 1.09 pg/m³) and 2015 (1.91 ± 0.77 pg/m³) decreased slightly but increased in 2017 (4.29 ± 1.24 pg/m³), while in winter, the mean concentrations of 1-NP gradually decreased 79.0% from 2010 (42.3 ± 16.1 pg/m³) to 2018 (8.90 ± 2.09 pg/m³). Table 2 also indicates that the 2-NP concentration variation was similar to that in 1-NP. However, the concentration of 2-NFR in PM$_{2.1}$ in summer was higher than that in winter in 2017/2018, which differed from 1-NP (Table 2). Previous studies also showed a similar result: the 2-NFR and/or 2-NP concentrations in cold seasons were lower than those in warm seasons in some Asian cities (Kameda et al., 2004). This occurs because the atmospheric 2-NFR and/or 2-NP depend not only on their parent PAH concentrations but also on meteorological conditions (temperature, solar radiation, etc.) and other air pollutants (NOx, O3, etc.) (Albinet et al., 2008).

### 2.2. Correlations between PAHs, NPAHs, and meteorological conditions

It has been previously reported that in addition to emission sources from human activities (local and/or external), the generation, accumulation, diffusion, removal, and phase partitioning of air pollutants are influenced by meteorological conditions (Amarillo and Carreras, 2016; Wang et al., 2016b). Table 3 summarizes the correlations between the meteorological conditions and the individual PAHs and NPAHs in PM$_{2.1}$ in the sampling periods.

Table 3 lists the significant negative correlations between the temperature and each individual PAH, 1-NP, and 2-NP (p < 0.05 and/or p < 0.01), indicating that the concentration was relatively high when the temperature was low. Appendix A Table S3 reveals that the mean temperature in winter was approximately 16 to 27°C lower than that in summer. It has been reported that PAHs with more than 4-rings can be transferred from the gaseous phase to the particle phase at relatively low ambient temperatures due to the low vapour pressure (Yamasaki et al., 1982). This was one of the reasons for the higher proportion of 4-ring PAHs in winter than in summer described in Section 2.1. On the other hand, the height of the mixed layer in Shanghai is relatively low and stable in winter, hindering the dispersion of air pollutants originating from human activities and thus resulting in high PAH concentrations (Gu et al., 2010).

Although previous studies reported that precipitation, relative humidity, and wind speed had negative correlations with air pollutants (Jiang et al., 2018; Kakimoto et al., 2000; Wang et al., 2016b), the data in Table 3 did not indicate any significant negative correlations with each individual PAH and NPAH in this study. This may have occurred because there was nearly no precipitation during the sampling periods in addition to summer in 2015 (Appendix A Table S3). Meanwhile, the variation in wind speed was not large in each sampling period in this study (Appendix A Table S3).

### 2.3. Emission sources of PAHs and NPAHs

The PAH diagnostic ratios are commonly used for the identification of potential emission sources, and several diagnostic ra-
Table 4 – Diagnostic ratios of PAHs and NPAHs in PM$_{2.5}$ from 2010 to 2018.

<table>
<thead>
<tr>
<th>Coal and/or biomass burning</th>
<th>Traffic emission</th>
<th>2010$^a$</th>
<th>2013</th>
<th>2015</th>
<th>2017/2018</th>
</tr>
</thead>
<tbody>
<tr>
<td>[FR]/[IPF] + [Pyr]</td>
<td>[BaA]/[BaA] + [Chr]</td>
<td>0.4 - 0.3$^a$</td>
<td>0.22 - 0.55$^b$</td>
<td>0.36 - 0.5$^c$</td>
<td>0.6 - 0.6$^d$</td>
</tr>
<tr>
<td>[BaA]/[BGPe]</td>
<td>&gt; 0.35$^b$</td>
<td>0.34</td>
<td>0.36</td>
<td>0.35</td>
<td>0.44</td>
</tr>
<tr>
<td>[IDP]/[IDP] + [BGPe]</td>
<td>&gt; 0.6$^d$</td>
<td>0.40</td>
<td>0.30</td>
<td>0.35</td>
<td>0.44</td>
</tr>
</tbody>
</table>

$^a$ Rogge et al., 1993
$^b$ Simcik et al., 1999
$^c$ Yang et al., 2019
$^d$ Yunker et al., 2002.

Table 5 – Loading of nine individual PAHs in PM$_{2.5}$ by principal component analysis in summer and winter periods$^a$.

<table>
<thead>
<tr>
<th>PC1</th>
<th>PC2</th>
<th>PC1</th>
<th>PC2</th>
</tr>
</thead>
<tbody>
<tr>
<td>FR</td>
<td>0.37</td>
<td>0.34</td>
<td>0.91</td>
</tr>
<tr>
<td>Pyr</td>
<td>0.37</td>
<td>0.89</td>
<td>0.86</td>
</tr>
<tr>
<td>BaA</td>
<td>0.69</td>
<td>0.50</td>
<td>0.53</td>
</tr>
<tr>
<td>Chr</td>
<td>0.74</td>
<td>0.64</td>
<td>0.71</td>
</tr>
<tr>
<td>BBF</td>
<td>0.54</td>
<td>0.67</td>
<td>0.50</td>
</tr>
<tr>
<td>BkF</td>
<td>0.92</td>
<td>0.32</td>
<td>0.88</td>
</tr>
<tr>
<td>BaP</td>
<td>0.74</td>
<td>0.39</td>
<td>0.89</td>
</tr>
<tr>
<td>BgPe</td>
<td>0.82</td>
<td>0.45</td>
<td>0.92</td>
</tr>
<tr>
<td>Variance %</td>
<td>84.4%</td>
<td>7.67%</td>
<td>85.3%</td>
</tr>
</tbody>
</table>

$^a$ High factor loadings (> 0.7) are marked in bold.

The most important reasons for the decreasing concentration of 4-ring PAHs in winter (Table 2), which mainly originate from incomplete coal burning (Harrison et al., 1996). Although the number of motor vehicles and the consumption of gasoline fuel and diesel oil have increased in recent years (Appendix A Table S4), the national standard for the emission limits for vehicles has become stricter. Specifically, the emission limit of PM was from 25 to 100 mg/km for different types of vehicles according to the national standard of the emission limits for light-duty vehicles issued in 2005 (GB18352.3–2005), while the emission limit was reduced to 4.5 mg/km for all types of vehicles in the new guideline issued in 2013 (GB18352.5–2013) and reduced to 3.0 mg/km in the newest guideline issued in 2016 (GB18352.6–2016). As shown in Table 2, the concentrations of 5- and 6-ring PAHs and 1-NP decreased in winter, indicating the positive effect of the new national standard because they easily originate from vehicle exhaust (Harrison et al., 1996; Tang et al., 2005). Comprehensive, in addition to the changes in energy consumption, such as reducing the use of fossil fuels, including coal, and increasing the use of clean energy, including natural gas, continually improving vehicle technology also controlled and reduced the emission of air pollutants, including PAHs and NPAHs in PM, from vehicle exhaust.

2.4. Backward trajectories

Backward trajectory analysis is used to determine the transport routes of the air mass (Tang et al., 2015; Yang et al., 2007, 2018; Zhang et al., 2020d). In this study, the results of the cluster analy-
sis of the backward trajectories in summer and winter are shown in Fig. 2. In summer (Fig. 2a–c), Shanghai is easily affected by air masses from the southern areas and the ocean, accounting for approximately 44% (cluster 1) and 55% (clusters 2 and 3) in 2013, 70% (clusters 1 and 2) and 30% (cluster 3) in 2015, and 94% (clusters 1, 2, and 3) and 6% (cluster 4) in 2017, respectively. In winter (Fig. 2d–f), most air masses come from the northern areas and surrounding areas, accounting for approximately 63% (clusters 2 and 3) and 38% (cluster 1) in 2013, 50% (clusters 2 and 4) and 18% (clusters 1 and 3) in 2015, and 40% (clusters 2 and 4) and 60% (clusters 1 and 3) in 2018, respectively. The air masses from the ocean can dilute some of the air pollutants in Shanghai (Liu et al., 2018; Wang et al., 2016b). Moreover, in addition to the influence of meteorological conditions described in Section 2.2, the residential heating systems in northern China released large amounts of PM from coal combustion (Ma et al., 2018), leading some PAHs and NPAHs in PM to be transported to Shanghai in winter. This was consistent with the previous study in which Liu et al. found that the relatively low concentration weighted trajectories towards Shanghai were in the southern areas and the ocean in summer and were in the central and northern areas in winter (Liu et al., 2018).

2.5. Health risks of PAHs and NPAHs

Table 6 summarizes the mean BaPeq concentrations and the ILCR from 2010 to 2018. In this study, the mean BaP concentrations were all below the limit of the daily 24-hr standard (2.5 ng/m³) regulated by the national ambient air quality standard (GB3095–2012) (MEE, 2012). The BaP concentration in winter decreased gradually and remained 5.0 to 11.1 times higher than that in summer, indicating a relatively higher cancer risk in winter. The ΣBaPeq concentrations also decreased in winter in recent years, similar to BaP. Table 6 indicates that BbF and IDP had the highest BaPeq concentrations except for BaP, suggesting relatively higher health risks than the other PAHs. Moreover, although the concentrations of 1-NP and 2-NFR were much lower than those of PAHs (Table 2), Table 6 shows that the BaPeq concentrations of 1-NP were comparable to those of FR and Pyr, and the BaPeq concentrations of 2-NFR were comparable to Chr and BgPe due to the relatively higher TEF values of 1-NP and 2-NFR (Table 1).

As revealed in Table 6, the mean ILCR was the highest in 2010 (9.12 × 10⁻⁹), which means that approximately 91 cancer cases can occur amongst one million people and gradually decreased; the ILCR in 2017/2018 was the lowest (4.81 × 10⁻⁹). Although the ILCR was one order of magnitude higher than the US EPA acceptable cancer risk level (10⁻⁶), the ILCR in this study was over-amplified for ordinary people because the URsair value used to calculate the ILCR was determined in an epidemiological study of coke-oven workers. Although the cancer risk in Shanghai still remains high, the decreasing trend in recent years suggests that the health risk of PAHs may foreseeably decrease in the future.

2.6. Research limitations

There were some limitations in the current research. Regarding sampling and source emission analysis, we did not collect gaseous samples, preventing the comparison of particle and gaseous phase PAHs and NPAHs. This also leads to some uncertainty in the diagnostic ratios and PCA results. Moreover, we did not analyse other US EPA priority PAHs, leading to some uncertainty in health risk assessment.

3. Conclusions

In this study, the regularly variations of the PM-bound PAHs and NPAHs in Shanghai over the past decade were first compared. The mean ΣPAHs and 1-NP concentrations in winter decreased by 39.7% and 79.0% from 2010 to 2018, respectively. BaF, BgPe, and 2-NFR were dominant compounds in all periods. The ambient
temperature was found to affect PM-bound PAH and NPAH concentrations. The emission sources in Shanghai were mainly affected by traffic emissions with some coal and/or biomass combustion. The OH radical-initiated reaction was the main pathway for the secondary formation of 2-NP and 2-NFR. Moreover, the air mass routes were different in each period, and the effect of external sources from northern China was greater in winter. On the other hand, the mean ZBaF₄ concentrations and ILCR in winter both decreased in recent years. A series of measures have been implemented to control air pollutant emissions from various sources in China in recent years. PAH and NPAH results in this study indicated the positive effects of various policies and regulations. However, the air pollution in winter is still severe. To further control and reduce air pollutant emissions, some measures should be strengthened. Examples include improving the combustion technology, such as increasing the combustion efficiency; popularizing the desulfurization and denitrification of fossil fuels; changing the energy structure, such as reducing the use of fossil fuels; popularizing clean and/or renewable energy; and using dust and smoke removal and condensation technologies to reduce some of the pollutants before entering the atmosphere. Moreover, the routes of exposure to PAHs and NPAHs include ingestion and dermal contact in addition to inhalation due to the characteristics of their generation and existence. Analysing simple and representative PAH and NPAH biomarkers can better evaluate the potential health risks of exposure to PAHs and NPAHs. However, the previous results of research on biomarkers, such as 1-hydroxyproline in human urine (Chetiyanukornkul et al., 2006; Kim et al., 2013), still showed some shortcomings because absorption, metabolism, and excretion may differ among PAHs and NPAHs and vary significantly among humans. We hope that we can provide basic data for finding better PAH and NPAH biomarkers through the accumulation of our data from atmospheric observations.

### Table 6 – Mean BaP-equivalent concentrations (pg/m⁴) and standard deviations of nine PAHs, 1-NP and 2-NFR in PM₂.₅ and inhalation lifetime cancer risk (ILCR) from 2010 to 2018.

<table>
<thead>
<tr>
<th></th>
<th>2010</th>
<th>2013</th>
<th>2015</th>
<th>2017/2018</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Summer</td>
<td>Winter</td>
<td>Summer</td>
<td>Winter</td>
</tr>
<tr>
<td>FR</td>
<td>0.11 ± 0.05</td>
<td>1.17 ± 0.65</td>
<td>0.14 ± 0.05</td>
<td>2.06 ± 1.29</td>
</tr>
<tr>
<td>Pyr</td>
<td>0.12 ± 0.05</td>
<td>0.96 ± 0.46</td>
<td>0.13 ± 0.04</td>
<td>1.86 ± 1.06</td>
</tr>
<tr>
<td>BaA</td>
<td>5.48 ± 2.04</td>
<td>98.6 ± 44.5</td>
<td>5.77 ± 2.83</td>
<td>67.5 ± 45.8</td>
</tr>
<tr>
<td>Chr</td>
<td>1.05 ± 0.45</td>
<td>17.4 ± 7.64</td>
<td>1.16 ± 0.37</td>
<td>16.4 ± 10.2</td>
</tr>
<tr>
<td>BaF</td>
<td>29.3 ± 7.69</td>
<td>214 ± 84.4</td>
<td>21.2 ± 9.66</td>
<td>210 ± 123</td>
</tr>
<tr>
<td>BK</td>
<td>11.1 ± 2.26</td>
<td>88.8 ± 30.5</td>
<td>7.19 ± 3.17</td>
<td>80.6 ± 47.2</td>
</tr>
<tr>
<td>BaP</td>
<td>151 ± 30.9</td>
<td>1270 ± 451</td>
<td>103 ± 45.1</td>
<td>1140 ± 734</td>
</tr>
<tr>
<td>RgPe</td>
<td>4.26 ± 1.28</td>
<td>21.8 ± 8.91</td>
<td>2.96 ± 1.38</td>
<td>25.3 ± 14.9</td>
</tr>
<tr>
<td>IDP</td>
<td>28.0 ± 9.04</td>
<td>145 ± 56.8</td>
<td>13.2 ± 6.15</td>
<td>136 ± 79.2</td>
</tr>
<tr>
<td>1-NP</td>
<td>0.63 ± 0.28</td>
<td>4.23 ± 1.61</td>
<td>0.35 ± 0.11</td>
<td>3.08 ± 1.54</td>
</tr>
<tr>
<td>2-NFR</td>
<td>0.15 ± 0.53</td>
<td>1.97 ± 0.78</td>
<td>0.11 ± 0.02</td>
<td>1.76 ± 0.69</td>
</tr>
<tr>
<td>ΣBaF₄eq</td>
<td>231 ± 52.7</td>
<td>1860 ± 645</td>
<td>155 ± 67.6</td>
<td>1690 ± 1050</td>
</tr>
<tr>
<td>ILCR</td>
<td>(9.12 ± 3.04) × 10⁻⁵</td>
<td>(8.00 ± 4.88) × 10⁻⁵</td>
<td>(5.65 ± 3.08) × 10⁻⁵</td>
<td>(4.81 ± 1.67) × 10⁻⁵</td>
</tr>
</tbody>
</table>

* Concentration data from Tang et al., 2013.

### Acknowledgments

This work was supported by the Ministry of Education, Culture, Sports, Science and Technology, Japan (17K08388); the Sasakawa Scientific Research Grant (2020–2028) from The Japan Science Society; the Environment Research and Technology Development Fund (5–1951) of the Environmental Restoration and Conservation Agency of Japan; the Sumitomo Foundation, Japan (182115); the CHUGEN Project of Kanazawa University, Japan; and the co-operative research programs of Institute of Nature and Environmental Technology, Kanazawa University, Japan (2006, 20062).

### Appendix A. Supplementary data

Supplementary material associated with this article can be found, in the online version, at doi:10.1016/j.jes.2020.06.017.

### REFERENCES


### Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.


