

Long-Term Trend of Polycyclic Aromatic 1 Hydrocarbon (PAH) Concentrations in Tokyo from 2007 to 2016: Effects of Changes in PAH Emissions and Degradation.

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1 **Long-term Trend of Polycyclic Aromatic Hydrocarbon (PAH)**
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3 **Changes in PAH Emissions and Degradation.**

4
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21 **Keywords:** PAHs; Central Tokyo; Increasing trend of ozone concentrations; PAH
22 Degradation

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24
25 **The concentrations of polycyclic aromatic hydrocarbons (PAHs) in aerosol were**
26 **measured in Shinjuku, which is central Tokyo, Japan, for 10 years from 2007 to**
27 **2016. The effects of changes in emission sources and their degradation by reaction**
28 **with ozone were assessed in this study. There was no significant increasing or**
29 **decreasing trend of the PAH concentrations during 10 years ($P > 0.05$). The**
30 **average selected seven the PAH concentrations (0.88 ng m^{-3}) during 10 years was**
31 **lower than those in New York and Paris. However, the trend of ozone**

32 concentrations is increasing in central Tokyo. This inconsistency raises a question.
33 Did the fact that the ozone concentration was higher than the PAH concentrations
34 promote PAH degradation? To apportion the PAH sources, we used PAH
35 concentration profiles and positive matrix factorization analysis. The contribution
36 of vehicle emissions to the PAHs ranged from 40 to 80 %. Ozone concentrations
37 increased by 3.70 %/year during 10 years. The theoretical degradation rates of
38 PAHs by ozone, which were calculated using a pseudo-first-order rate equation,
39 suggested that the lifetimes of benzo[*a*]pyrene (BaP) decreased by 1 min from 2007
40 to 2016. We investigated the aging of BaP using the profile of the isomer ratios. We
41 found that the aging of BaP at the urban and roadside sites were nearly identical
42 indicating aging regardless of the season. Although the decomposition of BaP is
43 promoted by the photochemical oxidation reaction, this result suggests that a
44 certain threshold value exists as the degree of the decomposition. This degradation
45 of PAH can improve chemical loss processes in air quality model.

46
47 Polycyclic aromatic hydrocarbons (PAHs) are carcinogenic and/or mutagenic chemical
48 component in PM_{2.5}.¹ The International Agency for Research on Cancer assigns
49 benzo[*a*]pyrene (BaP) to Group 1 (carcinogenic to humans).²

50 Recently, emission of air pollutants controls has been implemented based on the
51 national ambient air quality standards (NAAQSs) in representative megacities such as
52 Japan, the United States and Europe.^{3–5} One countermeasure against air pollution is
53 regulation of emissions from diesel vehicles.^{6,7} As a result, the concentrations of air
54 pollutants such as NO_x and PM_{2.5} in ambient air at roadside sites slightly have
55 decreased.^{7,8} On the other hand, although the trend of ozone concentrations is
56 decreasing in the United States and Europe, the trend is increasing at central Tokyo in
57 Japan.⁹ Titration of ozone by NO is low because of decreased NO_x concentration.
58 Consequently, the trend of ozone concentrations is increasing in central Tokyo.¹⁰ As
59 above, the ozone concentrations in central Tokyo has characteristics trend compared to
60 other countries such as New York and Paris, which are representative megacities in the
61 United States and Europe where emission controls have been implemented.

62 PAHs are rapidly degraded by ozone.^{11,12} Heterogeneous reaction of PAHs with
63 ozone is faster than the photochemical reactions.^{13,14} Long-term trends of atmospheric
64 PAH concentrations can be expected further the decreased PAH concentrations in
65 central Tokyo because high ozone concentration can promote PAH degradation.

66 We observed PAH concentrations for 10 years (2007–2016) in central Tokyo

67 (Shinjuku).

68 Herein, we describe our results on the change of long-term trends of PAH
69 concentrations in central Tokyo. In particular, we investigated the long-term trends of
70 BaP degradation with increasing ozone concentration in central Tokyo.

71

72 **RESULTS AND DISCUSSION**

73 **Annual variation of PAH concentrations (2007–2016)** In Shinjuku, measurements
74 were conducted during 40 weeks in four seasons from 2007 to 2016, and a total of 436
75 samples were collected. The annual average $\Sigma 7\text{PAH}$ and $\Sigma 15\text{PAH}$ concentrations, which
76 are defined as the sum of seven PAHs concentration and fifteen PAHs concentration,
77 respectively, are shown in Fig. 1. Detailed information about the observation periods
78 and the numbers of samples is shown in Table 1. The Mann–Kendall trend test¹⁵ showed
79 no significant increasing or decreasing trends ($P > 0.05$) of the PAH concentration data
80 over the course of the study period, although the average $\Sigma 7\text{PAH}$ and $\Sigma 15\text{PAH}$
81 concentrations spiked in 2015; suggesting that, there was little change in the PAH
82 concentrations over the course of the 10 years from 2007.

83 We compared the PAH concentrations in Shinjuku with them at megacities in the
84 United States and Europe, where emission controls have been implemented. The
85 average $\Sigma 8\text{PAH}$ concentration in New York City between 2001 and 2012 was 2.0 ng m^{-3} ,
86 1.6 and the PAH concentration measured in Paris since 2009–2010 using a
87 photoelectric aerosol sensor was 4.6 ng m^{-3} in summer and 13.8 ng m^{-3} in winter.¹⁷ The
88 $\Sigma 7\text{PAH}$ and $\Sigma 15\text{PAH}$ concentrations were 0.88 ng m^{-3} and 1.5 ng m^{-3} , respectively, and
89 both of them were lower than those in New York and Paris. In addition, we compared
90 the overall average BaP concentrations in Shinjuku with NAAQSs for BaP (Fig. 1).
91 There are no environmental standards for PAHs in Japan. However, in Europe,
92 NAAQSs for PAHs are defined. In Europe, the standard for annual average BaP
93 concentration is 1 ng m^{-3} .⁴ In United Kingdom, national air quality objective for annual
94 average BaP concentration is 0.25 ng m^{-3} .¹⁸ The overall average BaP concentrations
95 measured in our study ($0.05\text{--}0.29 \text{ ng m}^{-3}$) were also lower than the standard for annual
96 average BaP concentration (1 ng m^{-3}) in Europe (Fig.1).

97 Figure 2 show the long-term trends of the concentrations of anthropogenic trace
98 elements, namely Pd, Cd, Zn, Cu, Ni, Mn, Cr, and V in SPM with NO_x , ozone, and
99 $\text{PM}_{2.5}$ concentration at the observation points closest to our sampling site. Unlike the
100 PAH concentrations, the concentrations of anthropogenic trace elements, $\text{PM}_{2.5}$, and
101 NO_x tended to decrease from 2011 to 2016, at a rate of 25.3 %/year for the
102 anthropogenic trace elements (relative to the year 2011) and at rates of 3.87 %/year for

103 PM_{2.5} in this study period (relative to 2010) and 5.80 %/year and 5.63 %/year for NO_x in
104 the 10 years whole and this study period (relative to 2007). The decrease in NO_x
105 concentration is consistent with the long-term trend of NO_x concentration in the Kanto
106 region, as indicated by analysis of results obtained using the Community Multiscale Air
107 Quality model and NO_x observed from the satellite-based Ozone Monitoring
108 Instrument.¹⁹ These results reflect the effects of governmental measures aimed at
109 reducing vehicle emissions.²⁰

110 On the other hand, ozone concentrations increased gradually from 2007 to 2016
111 (2.00 %/year and 3.70 %/year in the 10 years whole period and overall period of this
112 study: OP) (Fig. 2), due to VOC limited in central Tokyo¹⁰ is considered as well as the
113 World Meteorological Organization (WMO) report.⁹ Although the trend of ozone
114 concentrations is decreasing in North America and Europe, the trend is increasing in
115 East Asia including at central Tokyo in Japan, in particular.⁹ Because ozone is consumed
116 by conversion of vehicle-discharged NO to NO₂ (Titration of ozone by NO), in
117 particular, recent reductions in NO_x emissions in central Tokyo can be expected to have
118 contributed to the increase in ozone concentrations.^{9, 10} In our study, the trend of ozone
119 concentrations also shows the same result based on the report of WMO and Kanaya et
120 al.^{9, 10} However, the time series of PAH concentrations was not consistent with those of
121 other air pollutants in this study.

122 This inconsistency raises several questions. Did the PAHs originate from a source
123 other than vehicles? Did the fact that the ozone concentration was higher than the PAH
124 concentrations promote PAH degradation? These two questions are discussed below.

125
126 **Source apportionment.** To determine whether the PAHs originated from a source
127 other than vehicles, we used (1) PAH concentration profiles and (2) PMF analysis to
128 apportion the PAH sources. (1) PAHs concentration profile to identify source factors in
129 PMF analysis, which are described in detail in the Supplement.

130
131 **PMF analysis to apportion the PAH sources.** We used the following three datasets
132 for PMF analysis: 15PAHs, 7PAHs, and PAHs+elements. To investigate the long-term
133 trend of the contribution ratio to each PAH sources during 10 years from 2007 to 2016,
134 we used the concentrations of 7 PAHs. However, we suspected that identifying PAH
135 sources by means of PMF might be difficult because of the lack of information on
136 sources of each PAHs. In order to use the dataset of 7 PAHs, we began by investigating
137 the common factors in PMF by comparing the results for the dataset of 15 PAHs with
138 the results for PAHs+elements. Moreover, using the procedure described by Han et al.,²¹

139 we compared the source profiles of the factors identified with the 15 PAHs dataset and
140 the factors identified with the dataset of PAHs+elements, either by inputting all the data
141 for a given year as a single file or by inputting the data for each observation period as a
142 separate file, with the goal of understanding the uncertainty of the PMF results. Details
143 regarding the identification of the factors are described in the Supplement.

144 Here, we verify whether 7 PAHs dataset could be used to investigate the long-term
145 trend of the contribution to each PAH sources by comparing results of 15 PAHs dataset
146 based on the common factors identified using PMF analysis.

147 We carried out a PMF analysis with 15 PAHs dataset in SPM collected from 2012 to
148 2016. This 15 PAH analysis identified five factors (Fig. S4). The dataset of 7 PAHs
149 collected from 2007 to 2016 were used in the PMF analysis, which identified four
150 factors (Fig. S8).

151 We compared gasoline vehicle emissions, diesel vehicle emissions, heavy oil
152 combustion, and waste incineration, which were identified as sources shared in common
153 by the datasets of 15 PAHs and the 7 PAHs. The factor profiles for the 7 PAHs dataset
154 were consistent with the profiles for the 15 PAHs dataset. Hence, we found that the
155 behaviors of both dataset before 2012 were consistent with each other. To better
156 understand the long-term trend of the PAH concentrations, we evaluated the trends of
157 the contributions of the major sources. Figure 3 shows variations of the contributions of
158 vehicle emissions (gasoline + diesel) for the datasets of 7 PAHs, 15 PAHs, and
159 PAHs+elements. Using the datasets of 7 PAHs and 15 PAHs, vehicle emissions
160 accounted for 40–80 % of the total PAHs. Whereas vehicle emissions contributed
161 20–50 % using the dataset of PAHs+elements. The contributions of vehicle emissions
162 using the datasets of PAHs+elements and 15 PAHs were similar from 2012 to 2016,
163 except for in 2015. The contribution of vehicle emissions showed no seasonal variation
164 (Fig. S10).

165 Therefore, the PAH concentration profiles and the PMF analysis indicated that the
166 PAHs observed from 2007 to 2016 originated mainly from vehicles. However, the
167 long-term trend of the PAH concentrations was affected by changes in the contributions
168 of decreased vehicle emissions (Fig. 2).

169

170 **Degradation of PAHs with ozone.** PAHs are rapidly degraded by photochemical
171 reactions.¹⁴ Heterogeneous reaction of PAHs with ozone is faster than the
172 photochemical reactions.^{13, 14} It was necessary to investigate the effect of ozone
173 concentration on PAH degradation. Because ozone concentration can be regarded as a
174 constant and can be included in an apparent PAH decay rate coefficient, the degradation

175 rate of PAH by ozone can be expressed by a pseudo-first-order rate equation under
176 constant temperature conditions^{11,22};

177

$$178 \quad \frac{d[\text{PAH}]}{dt} = -k'_1[\text{PAH}] \quad (1)$$

179

180 where $[\text{PAH}]$ is the concentration of a given PAH, and k'_1 is the pseudo-first-order
181 rate constant. Rate constant k'_1 depends strictly on ozone concentration:

$$182 \quad k'_1 = k_2[\text{O}_3] \quad (2)$$

183

184 where k_2 is a second-order rate constant. The value of k'_1 can be determined from the
185 following linear equation:

186

$$187 \quad \ln \frac{[\text{PAH}]}{[\text{PAH}]_0} = -k'_1 t \quad (3)$$

188

189 We investigated the relationship between k'_1 and ozone concentration. At low ozone
190 concentrations ($<5 \times 10^{12} \text{ cm}^{-3}$, ~ 200 ppb), k'_1 increases almost linearly with
191 increasing $[\text{O}_3]$, but at higher ozone concentrations, k'_1 becomes saturated at a value
192 designated as k'_{max} .¹¹ This behavior is a feature of the Langmuir–Hinshelwood
193 mechanism, which can be expressed in terms of the Pöschl–Rudich–Ammann model²³:

194

$$195 \quad k'_1 = k'_{\text{max}} \frac{K_{\text{O}_3}[\text{O}_3]}{1 + K_{\text{O}_3}[\text{O}_3]} \quad (4)$$

196

197 where K_{O_3} is the ozone-gas-to-surface equilibrium constant, and $[\text{O}_3]$ is the gas-phase

198 ozone concentration. Pöschl et al.¹¹ reported that the k'_{max} and K_{O_3} values for
199 heterogeneous reaction of BaP and ozone on soot are 0.015 s^{-1} and $2.8 \times 10^{-13} \text{ cm}^3$,
200 respectively.

201 The ozone concentration in Shinjuku increased gradually over the course of the study
202 period (Fig. 2), and the average ozone concentration in 2016 was approximately 6 ppb
203 (OP) higher than that in 2007. Because the average ozone concentrations observed in
204 this study period were low (13–25 ppb), it becomes linear in Eq. (4). At low ozone

205 concentrations, the pseudo-first-order rate constant varies considerably, and this
206 variation leads to large differences in PAH degradation rates. Under these conditions,
207 the atmospheric lifetimes of BaP during OP (Fig. 2) were calculated to be 13 min (OP)
208 in 2007 ($[O_3] = 13$ ppb (OP)) and 9 min (OP) in 2016 ($[O_3] = 19$ ppb (OP)) (Eq. (4));
209 that is, the lifetime was shorter in 2016 than that in 2007.

210 Mu et al.²⁴ reported that k'_1 increases almost linearly with increasing temperature. In
211 Tokyo, the annual mean temperature has risen in the 10 years since 2007²⁵ owing to the
212 heat island phenomenon. Hence, theoretically, PAHs could be expected to degrade
213 faster in 2016 than in 2007. However, in fact, the concentrations of BaP were almost
214 constant throughout the study period regardless of high or low ozone concentrations
215 (Fig. 1, Fig. S11).

216 We also evaluated the long-term trend of BaP concentrations during whole period in
217 spring and winter (Fig. S11). Normally, ozone concentrations in urban atmospheres are
218 highest in spring.²⁶ During our study period, the ozone concentration in the spring (35
219 ppb) exceeded the annual average (24 ppb) and was low (18 ppb) in winter. However,
220 we observed no differences between the spring and winter trends of PAH concentrations
221 (Fig. S11).

222 Here, we discuss the photochemical oxidation reaction using ANT/PHE and BaP/BeP
223 ratio. ANT and BaP are expected to be degraded more easily than their isomers during
224 transport.²⁷ Thus, high ANT/PHE and BaP/BeP ratios indicate relatively photochemical
225 aging processing. Although BaP/BeP is normally 1 in urban atmospheres, we found that
226 in Shinjuku, BaP/BeP deviated from 1 at the two sites in four seasons (Fig. 4). Low
227 ratios indicate aged PAHs.^{28, 29} Usually, these ratios are higher in winter and lower in
228 summer. However, at these two sites, these ratios were low and remained constant
229 regardless of the season. Although the decomposition of BaP is promoted by the
230 photochemical oxidation reaction, it is considered that a certain threshold value exists as
231 the degree of the decomposition. According to Brien et al.,³⁰ which investigated the
232 photolytic aging of secondary organic aerosol (SOA) in a laboratory experiment, there
233 is a certain threshold for its decomposition. Shimada et al.³¹ point out that the coating of
234 SOA is responsible for the existence of the BaP/BeP ratio threshold when transported
235 long distance from China to Okinawa, Japan. They suggests that degradation of PAHs
236 may have been suppressed by SOA coatings. Here, we should investigate the long-term
237 trends of decomposition, but unfortunately BeP measures only 2013 and 2014. At least
238 in central Tokyo, it is considered that photochemical oxidation reaction is promoted
239 more than in ordinary cities because of high ozone concentration. Thus, although the
240 PAH degradation in urban air in Shinjuku could theoretically have increased with the

241 increase in ozone concentration, the presence of an SOA coating may have shielded the
242 PAHs from ozone. Therefore, we suggest that the long-term trend of the PAH
243 concentrations was unlikely to have been affected by PAH degradation by reaction with
244 ozone.

245

246 **Implications**

247 We observed PAH concentrations in SPM for 10 years (from 2007 to 2016) in
248 Shinjuku, in central Tokyo. Investigating long-term trends of PAH concentrations in
249 Tokyo, where governmental measures against air pollutants have been implemented, can
250 be expected to improve our understanding of the health effects of air pollution. In this
251 report, we have described our results on the long-term trend of PAH concentrations and
252 the sources of the PAHs. PAH concentrations in urban air in Shinjuku did not change
253 during the study period and did not coincide with the trends of the concentrations of
254 other air pollutants. We suggest two possible explanations for these results: (1) Vehicles
255 were the main sources of the PAHs (accounting for 40 to 80 %), and there was no
256 significant change in the contribution of vehicle emissions to PAH concentrations
257 during the period from 2007 to 2016. (2) Although the decomposition of BaP is
258 promoted by the photochemical oxidation reaction, this result suggests that a certain
259 threshold value exists as the degree of the decomposition. In addition to physical loss
260 processes such wet and dry deposition, chemical degradation of PAH in this study can
261 improve chemical loss processes in air quality model.

262

263 **METHODS**

264 **Air sample collection** Samples for our study were collected at two sites in Shinjuku,
265 which has a population of 330,000. One site was an urban site located on the roof
266 (height, 51 m) of a building on the Nishi-Waseda campus at Waseda University; samples
267 were collected at this site from 2007 to 2016. The other site was a roadside site near the
268 campus, specifically Meiji Street, which is a main prefectural road with high volumes of
269 both diesel- and gasoline-engine vehicles (approximately 40,800 vehicles per day
270 according to a 2015 traffic census¹⁵). Samples were collected at the roadside site in
271 2015.

272 At both sites, SPM was collected on quartz fiber filters (8 × 10 in, 2500QAT-UP,
273 Pallflex) by means of high-volume air samplers (HV-1000F and HV-500F; Sibata,
274 Japan) equipped with an impactor (HV-RW/-1000R/-1000F, Sibata, Japan) stage to
275 eliminate particles with aerodynamic diameters more than 10 μm. The filters were
276 changed every 12 h (Daytime: 6:00 to 18:00, Nighttime: 18:00 to 6:00), and the flow
277 rate was 1 m³ min⁻¹. To remove organic matter prior to use, we pre-fired the filters at
278 600 °C in a muffle furnace for at least 6 h and then conditioned them in desiccators.

279 After sampling, the filters were stored in a freezer ($-20\text{ }^{\circ}\text{C}$) until analysis.

280

281 **Analysis of PAHs** PAHs were extracted from the quartz fiber filters as follows. Each
282 filter was inserted into a 50 mL brown sampling vial and extracted with 25 mL of
283 dichloromethane by ultrasonication (SineSonic2000 SINE, Tokyo, Japan) for 15 min
284 and then the solvent was decanted. This process was repeated three times. The
285 dichloromethane extracts were combined in a 300 mL flask and concentrated to a
286 volume of approximately 3 mL at 213–533 hPa and 305 K in a rotary evaporator
287 (RE400, Yamato, Tokyo, Japan). Insoluble particles were filtered from the concentrated
288 extract with a disposable syringe filter unit (DISMIS-25HP, Advantec, Tokyo, Japan).
289 Each filtrate was then placed in a 20 mL amber glass vial and evaporated to near
290 dryness under a gentle stream of dry nitrogen gas. As internal standards for evaluating
291 PAH signal intensities, a 100 μL isooctane solution containing a mixture of
292 acenaphthene- d_{10} and chrysene- d_{12} (5 ppm each) was added to each vial containing a
293 concentrated sample.

294 PAHs were analyzed by high-performance liquid chromatography on a system
295 consisting of a pump (LC-10AD, Shimadzu, Kyoto, Japan), a fluorescence detector
296 (RF-10AXL, Shimadzu, Kyoto, Japan), a system controller (SCL-10A, Shimadzu,
297 Kyoto, Japan), a degasser (DGU-20A₅, Shimadzu, Kyoto, Japan), an autosampler
298 injector (SIL-10AD, Shimadzu, Kyoto, Japan), a column oven (CTO-10A, Shimadzu,
299 Kyoto, Japan), and an analytical column (ZORBAX Eclipse PAH (3.0 ϕ ×250mm)

300 Agilent Technology, State of California, USA). The mobile phase was a 4:1 (v/v)
301 mixture of acetonitrile/water, and the flow rate was 0.5 mL min^{-1} . The following 15
302 PAHs, which had 3–6 rings, were analyzed by means of the selected-ion monitoring
303 method: acenaphthene (ACE), fluorene (FLU), phenanthrene (PHE), anthracene (ANT),
304 fluoranthene (FLT), pyrene (PYR), benz[*a*]anthracene (BaA), chrysene (CHR),
305 benzo[*b*]fluoranthene (BbF), benzo[*k*]fluoranthene (BkF), benzo[*e*]pyrene (BeP), BaP,
306 indeno[1,2,3-*cd*]pyrene (IcdP), DahA, and benzo[*ghi*]perylene (BghiP). Up until 2011,
307 we measured the concentrations of seven PAHs (ANT, FLT, PYR, BkF, BaP, IcdP, and
308 BghiP) and the fifteen PAHs were analyzed after 2012 (ACE, PHE, PYR, BaA, BaP,
309 BbF, BghiP (Sigma Aldrich, St. Louis, USA), ANT, BkF, IcdP (Wako Pure Chemical
310 Industries, Tokyo, Japan), FLT, DahA (Tokyo Kasei Kogyo, Tokyo, Japan), FLU (Kanto
311 Kagaku, Tokyo, Japan), BeP (Accu Standard, Connecticut, USA)). All chemicals were
312 used without further purification. The method detection limits ranged from 77.3 to 347
313 ng. A clean quartz blank filter was spiked with known amounts of the 15 PAHs to

314 determine recovery yields, which ranged from 79.2 to 98.7 %. Trace element analysis
315 and air pollutant data was described in in the Supplement.

316

317 **Positive Matrix Factorization Analysis** The positive matrix factorization (PMF)
318 model is a multivariate factor analysis tool that decomposes a matrix of speciated
319 sample data into two matrices: factor contributions and factor profiles. To identify the
320 source types that may contribute to the sample, the user must interpret the factor profiles
321 by using measured source profile information and emission or discharge inventories.³²

322 ³³ In this study, the US EPA PMF model (ver. 5.0) was used, and three types of PMF
323 analyses were performed. In the first analysis, we used the concentrations of seven
324 PAHs (7 PAHs: ANT, FLT, PYR, BkF, BaP, IcdP, and BghiP) and 436 samples as input
325 data. In the second, we used the concentrations of fifteen PAHs (15 PAHs: ACE, FLU,
326 PHE, ANT, FLT, PYR, BaA, CHR, BbF, BkF, BeP, BaP, IcdP, BghiP, and DahA) and
327 254 samples as input data. In the third, we used data for 21 species (Al, V, Cr, Mn, Fe,
328 Ni, Cu, Zn, Cd, Pb, As, FLT, PYR, BaA, CHR, BbF, BkF, BaP, IcdP, BghiP, and DahA)
329 and 254 samples as input data. We describe the source profile information in the
330 Supplement (Figs. S1–S3).

331 We selected the factor solution that had the most interpretable results, on the basis of
332 Sugiyama et al.³⁴; Miura et al.¹⁵ (Tables S1–S6). The criteria for choosing a factor
333 number were the interpretability of the factors and the results of error estimation. We
334 describe the procedure for error estimation in the Supplement.

335 The results of PMF analysis have uncertainty because the magnitude of the
336 contribution of a given major source may change during the study period. Thus, the
337 PMF model was applied to two datasets. First, the measurement results for all the
338 observation periods in a given year were used as a single dataset to estimate the major
339 factors. Second, the measurement results for the observation periods in a given year
340 were modeled separately (see Figs. S4–S10 in the Supplement).

341

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451

452 **Author Contributions**

453 K.S., M.N. and H.O designed the study. K.S., M.N. and H.O wrote the paper. K.S.,
454 M.N., K.M., T.U., Y.K., K.O., H.O., N.K., K.I., performed the experiments. K.S., M.N.,
455 K.M., T.U., Y.K., K.O., H.O., N.K., K.I., H.O. contributed to the sample collection. K.S.,
456 M.N., K.M., T.U., Y.K., K.O., H.O., N.K., K.I., H.O. contributed to the analysis of data
457 and discussions of the results. All authors read and commented on the manuscript.

458

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462 **ADDITIONAL INFORMATION**

463 **Competing interests:** The authors declare no competing interests.

464

465 Table 1. Sampling periods, numbers of samples, and $\Sigma 7\text{PAH}$ and $\Sigma 15\text{PAH}$
466 concentrations, 2007–2016.

467 Figure 1. Average annual ΣPAH and BaP concentrations, 2007–2016.

468 Figure 2. Average annual concentrations of (a) NO_x during 10 years whole ($y = -1.48x +$
469 35.6 , $R=0.815$) and this study period ($y = -1.09x + 32.7$, $R=0.68$), (b) $\text{PM}_{2.5}$ during this
470 study period ($y = -0.61x + 30.0$, $R=0.76$), (c) ozone during 10 years whole ($y = 0.47x +$
471 21.1 , $R=0.77$) and this study period ($y = 0.72x + 15.7$, $R=0.62$ except of 2008 year) (d)
472 anthropogenic elements during this study period, 2007–2016.

473 Figure 3. Contributions of vehicle emissions to 7 PAHs dataset, 15 PAHs dataset, and
474 PAHs+elements, 2007–2016.

475 Figure 4. PAH isomer ratios at the urban and roadside sites in 2015.

476

477 Table 1. Sampling periods, numbers of samples, and $\Sigma 7\text{PAH}$ and $\Sigma 15\text{PAH}$
478 concentrations, 2007–2016.

Observation period		No. of samples	$\Sigma 7\text{PAHs}$ (ng m^{-3})	$\Sigma 15\text{PAHs}$ (ng m^{-3})
2007	8/1–8/7	14	0.521	ND
2008	7/22–7/29	15	1.15	ND
2009	2/23–2/28	10	1.95	ND
	5/26–5/31	9	0.521	ND
	7/17–7/27	22	1.04	ND
	10/19–10/27	15	1.09	ND
2010	5/24–5/28	10	0.514	ND
	7/12–7/16	9	0.240	ND
	10/18–10/22	10	0.554	ND
	12/6–12/13	11	0.924	ND
2011	3/7–3/11	9	0.922	ND
	5/16–5/20	10	0.754	ND
	7/11–7/22	20	0.664	ND

	10/3–10/7	8	1.03	ND
	12/12–12/16	10	1.44	ND
2012	3/19–3/23	8	1.72	2.76
	5/14–5/18	9	1.25	1.88
	7/12–7/19	14	1.42	2.16
	8/17–8/24	12	0.773	1.28
	10/22–10/26	9	0.397	0.73
	12/3–12/7	10	0.889	1.53
2013	3/18–3/22	10	0.982	1.46
	5/13–5/17	9	1.29	1.97
	7/29–8/2	10	1.27	2.07
	8/15–8/22	13	0.481	0.761
	10/7–10/11	10	0.274	0.545
	12/2–12/6	9	1.89	2.69
2014	5/12–5/16	10	0.968	1.96
	7/13–7/19	13	0.899	1.76
	8/21–8/25	9	0.214	0.496
	10/20–10/24	10	1.43	2.75
	12/1–12/5	10	1.55	3.49
2015	4/6–4/10	10	1.17	1.90
	7/15–7/23	17	2.90	5.42
	8/18–8/21	6	3.11	6.29
	10/26–10/30	12	2.99	5.93
	11/30–12/4	10	2.44	6.24
2016	4/4–4/8	9	0.428	0.872
	7/12–7/15	7	0.390	0.629
	8/17–8/21	8	0.399	0.641

ND: no data

Figures

Figure 1

Average annual Σ PAH and BaP concentrations, 2007–2016.

Figure 2

Average annual concentrations of (a) NO_x during 10 years whole ($y = -1.48x + 35.6$, $R=0.815$) and this study period ($y = -1.09x + 32.7$, $R=0.68$), (b) PM_{2.5} during this study period ($y = -0.61x + 30.0$, $R=0.76$), (c) ozone during 10 years whole ($y = 0.47x + 21.1$, $R=0.77$) and this study period (y = 0.72x + 15.7, R=0.62 except of 2008 year) (d) anthropogenic elements during this study period, 2007–2016.

Figure 3

Contributions of vehicle emissions to 7 PAHs dataset, 15 PAHs dataset, and PAHs+elements, 2007–2016.

Figure 4

PAH isomer ratios at the urban and roadside sites in 2015.

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