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Source Apportionment of Gaseous and Particulate PAHs from Traffic Emission Using Tunnel Measurements in Shanghai, China

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1 **Source apportionment of gaseous and particulate PAHs from traffic**
2 **emission using tunnel measurements in Shanghai, China**

3
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12
13 **ABSTRACT**

14 Understanding sources and contributions of gaseous and particulate PAHs from
15 traffic-related pollution can provide valuable information for alleviating air
16 contamination from traffic in urban areas. On-road sampling campaigns were
17 comprehensively conducted during 2011-2012 in an urban tunnel of Shanghai, China.
18 2-3 rings PAHs were abundant in the tunnel's gas and particle phases. Diagnostic
19 ratios of PAHs were statistically described; several were significantly different
20 between the gas and particle phases. Principal component analysis (PCA), positive
21 matrix factorization (PMF), bivariate correlation analysis and multiple linear
22 regression analysis (MLRA) were applied to apportion sources of gaseous and
23 particulate PAHs in the tunnel. Main sources of the gaseous PAHs included evaporative
24 emission of fuel, high-temperature and low-temperature combustion of fuel,
25 accounting for 50-51%, 30-36% and 13-20%, respectively. Unburned fuel particles
26 (56.4-78.3%), high-temperature combustion of fuel (9.5-26.1%) and gas-to-particle
27 condensation (12.2-17.5%) were major contributors to the particulate PAHs. The

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28 result reflected, to a large extent, PAH emissions from the urban traffic of Shanghai.
29 Improving fuel efficiency of local vehicles will greatly reduce contribution of traffic
30 emission to atmospheric PAHs in urban areas. Source apportionment of PM₁₀ mass
31 was also performed based on the organic component data. The results showed that
32 high-temperature combustion of fuel and gas-to-particle condensation contributed to
33 15-18% and 7-8% of PM₁₀ mass, respectively, but 55-57% of the particle mass was left
34 unexplained. Although the results from the PCA and PMF models were comparable,
35 the PMF method is recommended for source apportionment of PAHs in real traffic
36 conditions. In addition, the combination of multivariate statistical method and
37 bivariate correlation analysis is a useful tool to comprehensively assess sources of
38 PAHs.

39

40 **Keywords:** Atmospheric pollution; Yan'an East Road tunnel; PM₁₀; PAHs; PMF; PCA;

41 **1 Introduction**

42 Globally urban ambient air pollution became a severe environmental problem,
43 which obviously impaired human health (Gehring et al., 2013). Recently smog hanging
44 over cities appears frequently in the cities of developing China, and it is the most
45 familiar and obvious reflection of air pollution. Many visible and invisible emissions
46 from human activities contribute to air pollution in urban atmosphere. One of the
47 main sources is road traffic pollution (Yin et al., 2010). For example, vehicular
48 emissions accounted for 40% of gaseous pollutants and 25% of total PM₁₀ within the
49 urban area of Guangzhou of China (Zhang et al., 2013). Vehicular exhaust ranked the
50 third (at 21%) most important source to carbonaceous particles in Shanghai (Cao et
51 al., 2013). Along with the urbanization of China, traffic-related pollution is likely to
52 become the largest contributor to urban air pollution (Shen et al., 2011).

53 Polycyclic aromatic hydrocarbons (PAHs) are typical persistent organic pollutants
54 stemming from incomplete combustion of organic materials, e.g., gasoline combustion
55 (Zhang et al., 2008). PAHs were selected as chemical tracers of traffic exhaust to
56 apportion air pollution in urban atmosphere in previous studies (Jamhari et al., 2014;
57 Khairy and Lohmann, 2013; Larsen and Baker, 2003; Yin et al., 2010). However, most
58 of source apportionment in previous works focused on urban-scale particles (Jamhari
59 et al., 2014; Khairy and Lohmann, 2013; Yin et al., 2010), few studies were
60 implemented in specific traffic environment, such as particles at the side of roads (Wu
61 et al., 2014) and in traffic tunnels (Lawrence et al., 2013). Traffic-related pollution of
62 PAHs is a mixed emission, including gasoline and diesel exhaust, fuel evaporation,
63 spillage of fuel and lube oil, wear and tear of brakes, tires and road surface materials,
64 re-suspension of road dusts, partitioning, condensation, among others
65 (Boonyatumanond et al., 2007; Harrison et al., 2003; Lawrence et al., 2013; Riddle et
66 al., 2008; Wu et al., 2014). Understanding specific sources and their contributions to
67 traffic-related pollution for the purpose of controlling and reducing traffic-related
68 emission in urban atmosphere is still novel and important for improving
69 environmental health. To our knowledge, few studies reported on source
70 apportionment of gaseous and particulate PAHs in a traffic environment. Source
71 apportionment was reported for a roadside environment using total concentration
72 (gaseous plus particulate) of PAHs as variables of principal component analysis
73 (Harrison et al., 2003).

74 Previous work ranked concentrations of sedimentary PAHs in Shanghai as low to
75 moderate on a global scale (Liu et al., 2008). PAH concentrations in rainwater (in
76 Shanghai) were also at the high end of worldwide figures (Yan et al., 2012).
77 Traffic-related pollution in Shanghai was considered as one of main PAH sources in air
78 (Wang et al., 2010), sediment (Liu et al., 2009), and soil (Liu et al., 2010). Gu et al.
79 (2010) suggested that diurnal variation of PM_{2.5} PAHs was related to the contribution
80 of vehicle emission in urban areas. Therefore, it is vital to comprehensively
81 understand PAH sources from traffic emission for reducing PAH contamination in
82 Shanghai.

83 Source apportionments based on receptor modeling in most published studies were
84 implemented via chemical mass balance (CMB) model and factor analysis methods, e.g.
85 principal component analysis (PCA), positive matrix factorization (PMF) and UNMIX
86 (Taiwo et al., 2014). Application of CMB model depends extremely on local profiles of
87 all sources, whereas multivariate statistical methods based on factor analysis do not
88 highlight a comprehensive knowledge of source composition (Pant and Harrison,
89 2012). However, the assignment of factors to specific source categories is highly
90 questionable in many cases due to disturbance from extreme data and genuine
91 collinearity of diverse sources (Larsen and Baker, 2003; Pant and Harrison, 2012).
92 Therefore, it is necessary to remove outliers from dataset and estimate
93 comprehensively sources factors represented when using multivariate statistical
94 methods to apportion sources. In this work, hierarchical cluster analysis (HCA) was
95 applied to screen outliers from dataset, and then multivariate statistical methods of
96 PCA and PMF were used to identify main sources of gaseous and particulate PAHs,
97 respectively. Finally bivariate correlation analysis was used to further confirm
98 chemical sources factors reflected via investigating correlation of factor scores from
99 PCA or factor contributions from PMF and other parameters, such as temperature, PM
100 content, organic carbon content.

101 The main objectives of this study include 1) characterizing profiles and diagnostic
102 ratios of gaseous and particulate PAHs in a typical urban tunnel of Shanghai; 2)
103 estimating the main PAH sources in the two phases; 3) quantifying their contributions
104 to the gaseous and particulate PAHs and PM₁₀ mass; and 4) comparing results of
105 source apportionment from PCA and PMF models. The results of this work provide
106 valuable information for development of effective control policies and measures to

107 decrease traffic-related air ambient contamination in urban area.

108

109 **2 Materials and methods**

110 **2.1 Sampling campaigns**

111 During 2011-2012, extensive sampling campaigns were carried out at the entrance
112 and exit of a typical urban traffic tunnel, the Yan'an East Road Tunnel in the city center
113 of Shanghai. Gasoline-powered vehicles dominated and accounted for >90% of total
114 vehicles in this tunnel. Two samplers were set up on inspection walkways, ~407 m
115 and ~490 m from the entrance and exit of the tunnel. The samplers' air inlets (PM₁₀)
116 were ~1.5 m above road surface and ~1 m away from edge of roadway. Gaseous and
117 particulate samples were collected with medium volume air samplers using quartz
118 fiber filters and XAD-2 resins. Traffic emissions of PAHs are combination of pyrogenic
119 and petrogenic PAHs. It is thus better to have short sampling times under different
120 operating conditions of tunnel so that collinearity of cases (similar contributions from
121 similar sources in a given sample) is minimized. Three campaigns, each lasting for 15
122 days or more, covered spring, autumn and winter. Sampling periods also included
123 daily and weekly variation. A total of 96 samples were collected in this study. More
124 details were described in the Supporting Information.

125

126 **2.2 Chemical analysis**

127 Gaseous and particulate PAHs were measured referring to the Method TO-13a
128 recommended by the US EPA(1999), including naphthalene (Nap), acenaphthylene
129 (AcNy), fluorene (Fl), acenaphthene (AcNe), phenanthrene (PhA), anthracene (An),
130 fluoranthene (FlA), pyrene (Py), benz[*a*]anthracene (BaA), chrysene (Chy),
131 benzo[*b*]fluoranthene (BbF), benzo[*k*]fluoranthene (BkF), benzo[*a*]pyrene (BaP),
132 benzo[*e*]pyrene (BeP), perylene (Pery), indeno[*1,2,3-cd*]pyrene (IP),
133 benzo[*ghi*]perylene (BghiP),and dibenz[*a,h*]anthracene (DBahA). Additionally, three
134 alkylated PAHs were measured, including methylnaphthalene (MNaP) and
135 methylphenanthrene (MPhA) and dimethylphenanthrene (DMPhA). Organic carbon
136 (OC) contents were determined. Carbon dioxide (CO₂) concentrations and
137 temperature (T) in the tunnel were recorded online. Quality assurance and quality
138 control (QA/QC) were periodically performed. See more details in the Supporting
139 Information.

140 **2.3 Data evaluation and modeling**

141 Before the statistical analysis of data, undetectable values were replaced by a
142 random number between zero and the limit of detection (LOD). PAHs with higher
143 molecular weight than chrysene were undetectable in most gaseous samples; these
144 gaseous concentrations were then removed from the dataset. Moreover, to determine
145 whether the dataset was suitable for multivariate statistical analysis, we performed
146 the Kaiser-Meyer-Olkin (KMO) and Bartlett's test of sphericity and required KMO's
147 value of greater than 0.7. High values (close to 1) usually indicate that the multivariate
148 factor analysis may be useful with the selected dataset. Hierarchical cluster analysis
149 (HCA) was applied to screen abnormal samples from dataset using weighted average
150 linkage between the groups and the Euclidean distance for the cluster intervals
151 (Kavouras et al., 2001). After removal of the anomalies, 80 samples remained for
152 multivariate statistical analysis, which meets the minimum number of samples
153 required for receptor modeling, namely a minimum variable to case ratio of 1:3
154 (Thurston and Spengler, 1985).

155 Multivariate statistical methods based factor analysis, PCA and PMF, are useful tools
156 to apportion sources (Larsen and Baker, 2003). In PCA, all factors with eigenvalues
157 over 1 were extracted and rotated using the Varimax method. Factor loadings and
158 scores of PCA were used to identify main sources and quantify their contributions,
159 respectively (Liu et al., 2009). In PMF analysis, the uncertainty file required included
160 the calculated LODs and recovery standard deviation of the surrogate standards
161 (Larsen and Baker, 2003) and the number of sources was set as the same as the PCA
162 model. The converged solution with the lowest Q (robust) value was selected for the
163 further investigation. More detail can be referred elsewhere (Norris et al., 2014).
164 Bivariate Pearson correlation analysis was applied for the purpose of exploring
165 potential relationship within sources, temperature, PM₁₀, OC and CO₂. Multiple linear
166 regression analysis (MLRA) was conducted using PCA factor scores or PMF factor
167 contributions and the standardized normal deviation of total PAHs concentrations in
168 the gas or particle phase and PM₁₀ mass (scaled to mean and standard deviation) as
169 independent and dependent variables, respectively. The regression was performed
170 using a forward stepwise method. The standardized regression coefficients were used
171 to calculate the relative contributions of major sources (Larsen and Baker, 2003; Liu et
172 al., 2009). PCA, MLRA, HCA and bivariate correlation analysis were performed using

173 SPSS statistical software packages (SPSS 13.0 for windows). The US EPA version of
174 PMF (PMF v5.0) was used in this work.

175

176 **3 Results and discuss.**

177 **3.1 Profiles of gaseous and particulate PAHs**

178 Profiles of average concentrations of gaseous and particulate PAHs at the entrance
179 and exit sampling sites are illustrated in Figure 1. Although PAH concentrations at the
180 exit of the tunnel are significantly ($p<0.01$) higher than those at the entrance, PAH
181 profiles are similar. In this study, 2-3 rings PAHs are abundant and dominated by
182 parent and alkylated naphthalene in the gas phase, while they are also abundant in the
183 particle phase. In other tunnel studies, the most abundant particle-phase PAHs were 4
184 rings PAHs, i.e., fluoranthene and pyrene (Ancelet et al., 2011; El Haddad et al., 2009;
185 Ho et al., 2009), or 5-6 rings PAHs, i.e., benzo[ghi]perylene and benzo[k]fluoranthene
186 (Chen et al., 2013). Many studies suggested diesel-vehicular or heavy-duty vehicle
187 emission were enriched in the low molecular weight PAH (≤ 4 rings), whereas, the high
188 molecular weight PAH were more abundant in gasoline engine or light-duty vehicle
189 emission (Ancelet et al., 2011; El Haddad et al., 2009; Kam et al., 2012). In the tunnel
190 of this study, heavy duty vehicles were restricted to pass except public transport buses
191 and gasoline-powered medium and light duty vehicles accounted for 91-98% by
192 manual counts based on tunnel traffic videos. The profiles of individual PAHs mainly
193 from gasoline engine emission in this study are different from previous reports (Lima
194 et al., 2005). Therefore, it is vital to comprehensively understand characters and
195 sources of PAHs in the real traffic environment.

196

197 **3.2 Diagnostic ratios of gaseous and particulate PAHs**

198 Isomer pairs are diluted, distributed and partitioned to a similar extent to
199 environmental receptors as they have almost identical physico-chemical properties.
200 Diagnostic ratios (DRs), including isomer ratios, indicate intra-source variability and
201 inter-source similarity, and provide an insight into source apportionment studies
202 (Tobiszewski and Namiesnik, 2012). DRs of gaseous and particulate PAHs at the
203 entrance and exit of the tunnel are statistically described in Table 1. As shown in Table
204 1, the DRs are comparable between the entrance and exit of the tunnel, and they
205 reflect characteristics of gasoline-powered vehicular emission under real traffic

206 conditions. It is worth noting that differences of alkylated and parent PAH DRs (i.e.,
207 $C_1/(C_0+C_1)$ NaP and $(C_1+C_2)/(C_0+C_1+C_2)$ PhA) between the entrance and exit are
208 statistically significant by the repeated measures one-way ANOVA test ($p<0.01$).
209 Incremented DRs are higher than the Entrance DRs and Exit DRs for particulate PAHs,
210 indicating more alkylated PAHs were released to the particle phase in the semi-closed
211 environment. As for gaseous PAHs, incremented DR of $(C_1+C_2)/(C_0+C_1+C_2)$ PhA, as
212 well as that in the particle phase, were also higher, whereas the incremented DR of
213 $C_1/(C_0+C_1)$ NaP was lower than the corresponding DRs. It implies that, more
214 naphthalene was released to the gas phase, or less gaseous alkylated naphthalene was
215 emitted in the tunnel. Therefore, the difference of sources and their contributions
216 should be further investigated by other methods in the following discussion.

217

218 **3.3 Source apportionment using multivariate statistical methods**

219 Outliers can severely distort representativeness of multivariate statistical analysis
220 result. In order to improve suitability of PAHs dataset for PCA and PMF and meet
221 requirement on KMO's value (>0.7), samples with outliers were screened by
222 hierarchical cluster analysis (HCA). HCA can cluster outliers (cases) as single member
223 or small cluster. After removal of the outliers, the KMO's values increased to 0.74 and
224 0.85 for the gaseous and particulate PAH datasets, respectively.

225 **3.3.1 Application of principal component analysis (PCA)**

226 The aim of PCA is to explain the maximum variability of original dataset with a
227 minimum number of factors. The factors reflect specific chemical sources of target
228 pollutants. As far as gaseous PAHs are concerned, 13 chemicals are included in the
229 PCA model, from naphthalene (2 rings) to chrysene (4 rings). In Table 2, three factors
230 extracted account for 83% of variability in the dataset. Factor PCA_G_1, contributing
231 37% of total variance, is dominated by AcNy, Fl, PhA, An and FlA. High loadings of
232 MNaP, MPhA and DMPPhA and medium loadings of NaP and FlA and Py are observed in
233 Factor PCA_G_2 which explains 29% of the variance. Factor PCA_G_3 (17% of the
234 variance) is highly weighted by BaA and Chy. As for particulate PAHs, three principal
235 components contain 21 chemicals, explaining 83% of total variance in Table 2. Factor
236 PCA_P_1 (33% of total variance) is dominated by BaA, Chy, BbF, BkF, BeP, BaP, Pery, IP
237 and DBahA. High loadings of MNaP, AcNy, AcNe, Fl and PhA and medium loadings of
238 NaP, MPhA and DMPPhA are observed in Factor PCA_P_2, accounting for 28% of the

239 variance. Factor PCA_P_3 (22% of the variance) is highly weighted by An, FlA and Py,
240 and moderately by MPhA, DMPPhA, BaA and Chy.

241 Anthropogenic PAHs in the atmospheric environment commonly originate from
242 petrogenic and pyrogenic sources. The former are generated from combustion
243 procedure of organic matters under oxygen-deficient conditions (Ravindra et al.,
244 2008), including wood, fossil fuel etc., while petroleum products, e.g., gasoline and
245 diesel, contain petrogenic PAHs and are emitted into air by evaporation. Incomplete
246 combustion of gasoline and diesel emits exhaust mixing with petrogenic and
247 pyrogenic PAHs (Wallington et al., 2006). Alkylated PAHs were considered as
248 indicators of petrogenic sources of PAHs due to the fact they are abundant in fuel oils
249 (Dobbins et al., 2006) and eliminated in combustion process (Rhead and Hardy, 2003).
250 Hence, Factor PCA_G_2 and PCA_P_2 are assigned to petrogenic source, e.g.,
251 evaporative emission of fuel, unburned fuel or lube oil.

252 Low molecular weight PAHs are emitted during low temperature combustion
253 processes, whereas high temperature processes form higher molecular weight PAHs
254 (Tobiszewski and Namiesnik, 2012). Increased driving speed usually leads to higher
255 temperature of the exhaust gas (Giechaskiel et al., 2005; Kittelson et al., 2004), and
256 vice-versa lower combustion temperature of fuel results from idling conditions (Ji and
257 Wang, 2010). Therefore, Factor PCA_G_1, PCA_G_3, PCA_P_1 and PCA_P_3 are assigned
258 to pyrogenic sources with different combustion temperatures. The combustion
259 temperature of Factor PCA_G_3 was probably higher than that of Factor PCA_G_1.
260 Similarly, the temperature of Factor PCA_P_1 was higher than that of Factor PCA_P_3.
261 Furthermore, low loadings of alkylated PAHs in Factor PCA_G_1, PCA_G_3 and PCA_P_1
262 also indicate that they mainly originated not from petrogenic but from pyrogenic
263 process. Different from them, however, medium loadings of MPhA (0.58) and DMPPhA
264 (0.69) in Factor PCA_P_3 imply that the source also contained petrogenic contribution
265 to a large extent. Therefore, Factor PCA_P_3 is considered as a mixing source
266 containing pyrogenic and petrogenic PAHs.

267 In addition, medium positive loadings of naphthalene (0.58 and 0.50) are found in
268 Factor PCA_G_2 and PCA_G_3, implying that chemical sources represented by the two
269 emitted simultaneously gaseous naphthalene. This result is consistent with what was
270 observed in diagnostic ratios of $C_1/(C_0+C_1)$ Nap, further indicating more emission of
271 gaseous naphthalene in the tunnel and its formation possibly from pyrogenic

272 procedure (Factor PCA_G_3).

273

274 **3.3.2 Application of positive matrix factorization (PMF)**

275 PMF is a powerful multivariate technique that constraints the solution to be
276 non-negative and takes into account the uncertainty of the observed data (Paatero and
277 Tapper, 1994), and was strongly recommended for use in comparison to PCA (Pant
278 and Harrison, 2012). The factor profiles of gaseous and particulate PAHs from the PMF
279 model are shown in Table 3. The profiles in Table 3 are completely comparable and
280 parallel with the factor loadings from PCA in Table 2. The only differences to point out
281 are naphthalene (NaP), acenaphthylene (AcNy) and Benzo[ghi]perylene (BghiP). The
282 loadings of Nap are almost zero in the factors of PCA_G_1 and PCA_P_3 in Table 2,
283 while all factors from PMF in Table 3 contain NaP more or less. Naphthalene was
284 detected commonly in most of PAH sources. Most of AcNy and BghiP are attributed to
285 Factor PMF_P_1 (pyrogenic source) in the PMF model, whereas in the PCA model most
286 of AcNy belong to Factor PCA_P_2 (petrogenic source) and BghiP is almost equally
287 separated into Factor PCA_P_1 (pyrogenic source) and PCA_P_3 (mix source). AcNy
288 and BghiP were identified as indicators of vehicle exhaust (Larsen and Baker, 2003;
289 Simcik et al., 1999). Hence, the result from the PMF model is more reasonable than
290 that from the PCA model. The subtle difference in sources profiles between PCA and
291 PMF is analyzed further in the following source estimates.

292

293 **3.3.3 Source estimates by bivariate correlation analysis.**

294 Bivariate correlation analysis is a useful tool to determine the empirical relationship
295 for the purpose of testing hypotheses of association and causality. In the study,
296 bivariate analysis is performed to explore the correlation among each factor scores of
297 PCA, factor contributions of PMF, temperature, CO₂, PM₁₀, OC, total concentration of
298 particulate PAHs (PM TPAHs) and gaseous PAHs (Gas TPAHs). The Pearson's
299 correlation coefficients are listed in Table S1. The empirical relationships are used to
300 further estimate chemical sources represented by these factors.

301 Strongly significant positive correlations (marked double asterisks in Table S1)
302 were observed amongst each other between tunnel temperature, CO₂, PM₁₀, OC, and
303 gaseous total PAHs (Gas TPAHs). This indicated that gasoline combustion emitted
304 carbon dioxides, suspended particles, hydrocarbons and gaseous PAHs, and

305 meanwhile released a large amount of heat increasing the temperature. Fuel
306 evaporation is an important emission path of petrogenic PAHs and the emissions are
307 higher at higher ambient temperature (Khairy and Lohmann, 2013; Pang et al., 2014).
308 PCA_Gas_FS_2 was significantly positively correlated with tunnel temperatures and
309 Factor PCA_G_2 was the one and only petrogenic source of gaseous PAHs in the PCA
310 model. Hence, the factor is considered as evaporative emission of fuel. Compared with
311 PCA_Gas_FS_2, no significance of correlation between the temperatures and
312 PCA_PM_FS_2 (Factor PCA_P_2 is main petrogenic source of particulate PAHs) implies
313 the different petrogenic sources between the gas and particle phases. A possible
314 reason is that droplets of unburned fuel or lube oil in internal combustion engine were
315 directly emitted to the particle phase.

316 PCA_PM_FS_3 was strongly significantly correlated with Gas TPAHs (0.36) and
317 Factor PCA_P_3 has been assigned to mixing source contained petrogenic and
318 pyrogenic PAHs in the PCA model. In the vehicular tailpipe where temperatures were
319 high, most of the volatile materials were in the gas phase. In diluting and cooling
320 processes, the relative amounts of materials, including gaseous PAHs, nucleate to form
321 new particles, condensed and absorbed onto existing particles (Kittelson, 1998). The
322 transformation from gas to particle phase was widely observed in urban atmosphere
323 as accumulation mode of particulate PAHs (Zhang et al., 2012). Strongly significant
324 positive correlation between the factor score and OC (0.67) and PM₁₀ (0.30) were also
325 observed in Table S1. Therefore, Factor PCA_P_3 probably reflects the gas-to-particle
326 condensation of PAHs.

327 Bivariate correlation results based on the PMF factor contributions were
328 comparable to a large extent with those based on the PCA factor scores. Factor
329 contributions in the PMF model were significantly positively correlated with factor
330 scores in the PCA model at the 0.01 level. The strongly significant correlations
331 mentioned above in the PCA model were also observed in the PMF model, indicating
332 the sources identified based on the two models are, by and large, consistent. However,
333 subtle differences between PCA and PMF are clearly shown in Table S1. The factor
334 scores from the PCA model are orthogonal to each other (Pearson correlation
335 coefficient = 0), whereas Table S1 shows strongly significant negative correlation
336 (-0.29) between PMF_Gas_FC_1 and PMF_Gas_FC_3 and strongly significant positive
337 correlation (0.64) between PMF_PM_FC_1 and PMF_PM_FC_2. In the PCA model, the

338 orthogonal factor scores result mainly from the Varimax rotation of extracted factors,
339 probably leading to conceal the co-variation of sources in real cases. The negative
340 correlation of factor contributions from the PMF model reflects the inverse
341 relationship between high-speed and low-speed traffic conditions of the tunnel, due to
342 high-temperature combustion of fuel (PMF_G_3) at high-speed driving condition while
343 low-temperature combustion (PMF_G_1) at low-speed driving condition (i.e.,
344 idling)(Giechaskiel et al., 2005; Kittelson et al., 2004). Likewise, the positive
345 correlation demonstrates the co-emission of high-temperature combustion exhaust
346 (PMF_P_1) and unburned fuel particles (PMF_P_2) in the particle phase.

347 The strongly significant negative correlation between emissions from
348 low-temperature combustion (G_1) and unburned fuel particles (P_2) is found in the
349 PCA model (-0.32), but not in the PMF model (-0.16), possibly suggesting that the
350 association is questionable in the PCA model. In addition, strongly significant positive
351 correlations between evaporative emission of fuel (G_2) and PM₁₀ (0.50 and 0.46) and
352 OC (0.46 and 0.43) were all observed in the two models, but it was difficult to
353 reasonably explain the associations based on our present understanding. Other
354 differences and similarities of significance are also observed in the two models. More
355 information should be added in the future investigation.

356 In summary, both of the multivariate statistical methods can identify the main
357 sources of the gaseous and particulate PAHs, but the PMF results are easier to
358 interpret and explain than those from the PCA model in this study.

359

360 **3.3.4 Source contributions to PAHs using multiple linear regression analysis**

361 After estimating the main sources of gaseous and particulate PAHs in the traffic
362 tunnel, source contributions were quantified by multiple linear regression analysis
363 (MLRA) with PCA factor scores or normalized PMF factor contributions and
364 normalized total PAH concentrations as independent and dependent variables,
365 respectively. The MLRA was widely applied to apportion sources of PAHs in sediments
366 (Liu et al., 2009), urban atmosphere (Larsen and Baker, 2003) and tunnel air
367 (Lawrence et al., 2013).

368 Table 4 presents the standardized regression coefficients (B) and calculated source
369 contributions of gaseous and particulate PAHs. Determination coefficients (R square)
370 of 74-98% indicated a good fit and successful application of MLRA. As for gaseous

371 PAHs, the overall source contributions compared well between the two models. The
372 first contributor was evaporation emission of fuel, accounting for 50-51% of the mass.
373 The following two were pyrogenic sources, accounting for 30.4-35.8% (Factor G_3)
374 and 13.4-19.6% (Factor G_1), respectively. The former represented
375 higher-temperature combustion of fuel, while the latter reflected lower-temperature
376 combustion of fuel. As far as particulate PAHs are concerned, unburned fuel particle
377 was the largest contributor of particulate PAHs and accounted for 56.4-78.3% of the
378 mass. The remaining were high-temperature combustion of fuel (9.5-26.1%) and
379 gas-to-particle condensation (12.2-17.5%). In the PCA model, the contributions of
380 petrogenic sources were 50-56% of total PAHs, in both the gas and particle phases. By
381 contrast, the contribution of petrogenic source was obviously higher in the particle
382 phase (78.3%) than (56.4%) in the gas phase in the PMF model, which was generally
383 consistent with the results from diagnostic ratios. The source contributions based on
384 the PMF model seemed to be more credible than the PCA results in this case.

385 As a consequence, the petrogenic sources, e.g., evaporative emission and unburned
386 fuel particles, were the biggest contributors of total PAHs in the gas and particle
387 phases. We acknowledge this study cannot reflect on total PAHs emission from local
388 traffic. As a typical urban traffic channel, results from this tunnel can, to a large extent,
389 be reasonably extended to the local traffic environment. Controlling emission from
390 petrogenic sources is the most principal task for the purpose of decreasing local urban
391 PAH contamination from traffic emission. Improving fuel efficiency will greatly reduce
392 contribution of traffic emission to atmospheric PAHs. In addition, the contribution of
393 secondary organic aerosol (e.g., gas-to-particle condensation) should not be ignored.

394

395 **3.3.5 Source contributions to PM₁₀**

396 The MLRA also tentatively explored to apportion sources of PM₁₀ using PCA factor
397 scores or normalized PMF factor contributions and normalized PM₁₀ contents as
398 independent and dependent, respectively. Regression results are presented in Table 5.
399 Stepwise algorithm chooses factor scores of G_2, P_1 and P_3 as predictors in the two
400 models. The standardized coefficients (B) indicate the relative importance of the
401 significant predictors. Evaporative emission of fuel (Factor G_2) contributes 20% of
402 PM₁₀ mass. Their direct causality is hard to be explained; the result originates
403 probably from the strongly positive significant correlation between PM₁₀ and factor

404 score of G_2 in the two models, as shown in Table4. However, a potential indirect
405 causality or an unknown transformation of particulate matter should not be safely
406 ignored.

407 High-temperature combustion of fuel (Factor P_1) emits 15-18%, and the
408 gas-to-particle condensation (Factor P_3) forms 7-8% of the PM₁₀. More than half of
409 variation (55-57%) in PM₁₀ mass is yet unexplained based on the two models,
410 indicating that the selected PAHs are of the limited source tracers of PM₁₀ in the tunnel.
411 Since particulate matters consist of inorganic (trace metals, cations and anions) and
412 organic species, adding metal data to the organic component dataset probably
413 decrease the unexplained contribution to PM₁₀ mass (Harrison et al., 2003; Lawrence
414 et al., 2013). As a result, the dataset only including organic component data is not
415 recommended to apportion source of PM₁₀ mass.

416

417 **4 Conclusions**

418 In the urban tunnel of Shanghai, 2-3 rings PAHs were abundant in the gas and
419 particle phases. The main sources of gaseous PAHs included evaporative emission of
420 fuel, high-temperature and low-temperature combustion of fuel. Their contributions
421 were 50-51%, 30-36% and 13-20%, respectively. Unburned fuel particle,
422 high-temperature combustion of fuel and gas-to-particle condensation were major
423 contributors of particulate PAHs in the tunnel, accounting for 56.4-78.3%, 9.5-26.1%
424 and 12.2-17.5%, respectively. Due to the results reflected to a large extent PAH
425 emission in urban traffic of Shanghai, it seems to be logical to deduce that improving
426 fuel efficiency of local vehicles will greatly reduce contribution of traffic emission to
427 atmospheric PAHs in urban area. Contributions of high-temperature combustion of
428 fuel and gas-to-particle condensation accounted for 15-18% and 7-8% of the PM₁₀
429 mass, respectively. But yet 55-57% of the PM₁₀ was unexplained in the present
430 condition. The dataset only containing organic component dataset was not
431 recommended to apportion source of PM₁₀ mass. Although source profiles were
432 extremely parallel based on the PCA and PMF models, source contributions to PAHs
433 from the PMF results were more credible than that from the PCA model. Consequently,
434 the PMF method is strongly recommended for use. Bivariate correlation analysis can
435 be considered as one of complementary tools of the factor analysis.

436

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446

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561

562

Table 1. Average, 25th and 75th percentiles of diagnostic ratios (DRs) of gaseous and particulate PAH at the entrance and exit of the tunnel.

Diagnostic Ratios	Particulate PAHs			Gaseous PAHs		
	Entrance DR	Exit DR	Incremented DR ^a	Entrance DR	Exit DR	Incremented DR
$C_1/(C_0+C_1)NaP$	0.61(0.50-0.75)	0.63(0.55-0.76) ^b	0.66(0.43-0.86)	0.33(0.29-0.36)	0.31(0.27-0.33) ^b	0.29(0.24-0.32)
$(C_1+C_2)/(C_0+C_1+C_2)PhA$	0.54(0.51-0.61)	0.60(0.55-0.67) ^b	0.70(0.62-0.79)	0.30(0.20-0.39)	0.35(0.27-0.42) ^b	0.53(0.42-0.65)
$An/(An+PhA)$	0.07(0.04-0.10)	0.06(0.04-0.08)	0.08(0.02-0.10)	0.13(0.10-0.16)	0.13(0.10-0.15)	0.13(0.09-0.16)
$FIA/(FIA+Py)$	0.49(0.47-0.53)	0.47(0.44-0.53)	0.49(0.36-0.58)	0.59(0.58-0.61)	0.58(0.57-0.60)	0.56(0.45-0.62)
$BaA/(BaA+Chy)$	0.32(0.30-0.34)	0.31(0.29-0.33)	0.33(0.26-0.37)	0.32(0.26-0.37)	0.33(0.29-0.35)	0.34(0.20-0.43)
$BaP/(BaP+BeP)$	0.37(0.34-0.41)	0.35(0.32-0.39)	0.31(0.19-0.37)	-	-	-
$IP/(IP+BghiP)$	0.40(0.38-0.47)	0.38(0.31-0.46)	0.37(0.18-0.50)	-	-	-

^a, incremented DRs are based on incremented PAHs between the exit and entrance of the tunnel;

^b, the repeated measures one-way ANOVA results showed that DRs were significantly ($p=0.01$) higher or lower at the exit than at the entrance.

Table 2. Factor loadings of gaseous and particulate PAHs in the PCA model.

No.	PAH	Gaseous PAHs			Particulate PAHs		
		PCA_G_1	PCA_G_2	PCA_G_3	PCA_P_1	PCA_P_2	PCA_P_3
1	NaP	0.00	<i>0.58</i>	<i>0.50</i>	0.16	<i>0.67</i>	-0.06
2	MNaP	0.29	0.74	0.27	0.39	0.88	0.02
3	AcNy	0.86	-0.11	0.20	0.44	0.72	0.14
4	AcNe	<i>0.67</i>	0.40	0.29	0.43	0.84	0.18
5	Fl	0.93	0.13	0.11	0.42	0.86	0.19
6	PhA	0.87	0.40	-0.04	0.31	0.77	0.45
7	An	0.93	0.12	-0.15	0.16	0.15	0.77
8	MPhA	0.28	0.92	0.15	0.26	<i>0.68</i>	<i>0.58</i>
9	DMPHA	0.07	0.93	0.23	0.21	<i>0.59</i>	<i>0.69</i>
10	FlA	0.75	<i>0.54</i>	-0.10	0.25	0.09	0.91
11	Py	<i>0.66</i>	<i>0.63</i>	-0.08	0.20	-0.08	0.91
12	BaA	0.03	0.12	0.93	0.72	0.16	<i>0.53</i>
13	Chy	0.04	0.27	0.90	0.70	0.24	<i>0.53</i>
14	BbF				0.87	0.34	0.29
15	BkF				0.79	0.47	0.17
16	BeP				0.78	0.34	0.44
17	BaP				0.81	0.46	0.29
18	Pery				0.70	0.45	0.33
19	IP				0.82	0.30	0.26
20	DBahA				0.77	0.32	-0.09
21	BghiP				<i>0.61</i>	0.37	<i>0.51</i>
Estimated source		Pyrogenic	Petrogenic	Pyrogenic	Pyrogenic	Petrogenic	Mix
Variance (%)		37	29	17	33	28	22

a Rotation method: Varimax with Kaiser normalization.

b Bold loadings > 0.70, Italic loading > 0.50.

c KMO's test results are 0.741 and 0.854 for gaseous and particulate PAHs.

Table 3. Factor profiles (% of species total) of gaseous and particulate PAHs in the PMF model.

No.	PAH	Gaseous PAHs			Particulate PAHs		
		PMF_G_1	PMF_G_2	PMF_G_3	PMF_P_1	PMF_P_2	PMF_P_3
1	NaP	17.6	50.1	32.3	21.4	<i>44.5</i>	<i>34.0</i>
2	MNaP	28.6	<i>49.7</i>	21.7	7.5	92.5	0.0
3	AcNy	73.1	2.8	24.1	53.3	<i>37.8</i>	9.0
4	AcNe	<i>44.9</i>	29.3	25.8	8.7	85.7	5.6
5	Fl	67.1	13.4	19.6	7.3	78.6	14.2
6	PhA	58.4	26.4	15.3	7.8	51.0	41.2
7	An	79.5	9.3	11.2	0.5	15.1	84.5
8	MPhA	19.2	63.5	17.3	20.5	<i>44.4</i>	<i>35.1</i>
9	DMPHA	2.1	76.7	21.2	21.3	<i>34.7</i>	<i>44.0</i>
10	FlA	<i>49.1</i>	<i>34.5</i>	16.3	22.2	4.9	72.8
11	Py	<i>43.9</i>	<i>40.8</i>	15.3	20.0	1.4	78.6
12	BaA	1.2	0.0	98.8	69.8	3.9	26.3
13	Chy	0.0	15.0	85.0	71.5	0.2	28.2
14	BbF				85.6	3.6	10.7
15	BkF				88.5	9.0	2.6
16	BeP				73.0	10.4	16.6
17	BaP				80.7	13.4	5.8
18	Pery				58.8	17.9	23.3
19	IP				83.8	10.6	5.6
20	DBahA				82.2	14.9	2.8
21	BghiP				79.6	7.1	13.2
Estimated source		Pyrogenic	Petrogenic	Pyrogenic	Pyrogenic	Petrogenic	Mix

a**Bold** percentage > 50%, and *Italic*> 30%.

Table 4. Source apportionment of gaseous and particulate PAHs in the tunnel based on the models of PCA and PMF.

Factor	Gaseous PAHs					Particulate PAHs				
	Sources	PCA		PMF		Sources	PCA		PMF	
		B	Contribution	B	Contribution		B	Contribution	B	Contribution
1	Low-temp. combust.	0.272	19.6%	0.230	13.4%	High-temp. combust.	0.401	26.1%	0.107	9.5%
2	Evaporation	0.695	50.0%	0.874	50.8%	Unburned fuel particle	0.866	56.4%	0.878	78.3%
3	High-temp. combust.	0.422	30.4%	0.616	35.8%	Condensation	0.269	17.5%	0.137	12.2%
		<i>(R² = 0.74)</i>		<i>(R² = 0.90)</i>		<i>(R² = 0.98)</i>		<i>(R² = 0.91)</i>		

Table 5. Source apportionment of the PM₁₀ mass in the tunnel based on the models of PCA and PMF.

Factor	Sources	B	Contribution
<i>(PCA model)</i>			
G_2	Evaporation	0.494	20%
P_1	High-temp. combus.	0.385	15%
P_3	Condensation	0.205	8%
	Unexplained		57%
	(R ² = 0.43)		
<i>(PMF model)</i>			
G_2	Evaporation	0.523	20%
P_1	High-temp. combus.	0.467	18%
P_3	Condensation	0.180	7%
	Unexplained		55%
	(R ² = 0.45)		

FIGURE CAPTIONS

FIGURE 1. Profiles of average concentrations of gaseous and particulate PAHs at the entrance and exit sampling locations of the tunnel.