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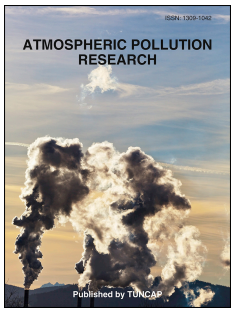

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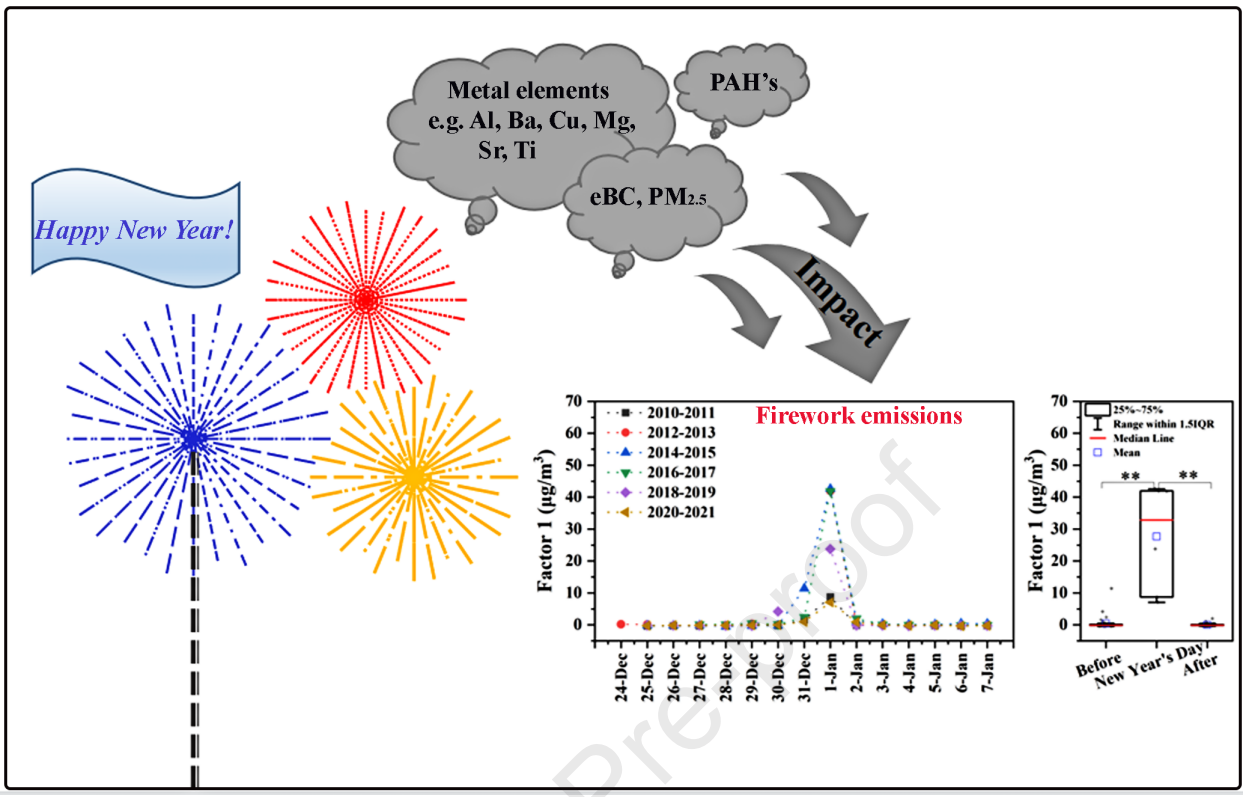
CRediT authorship contribution statement

Mohamed Khedr: Data curation, Methodology, Writing original draft. Xiansheng Liu: Data curation, Methodology, Software, Writing original draft. Hadiatullah Hadiatullah: Methodology, Software, Writing original draft. Jürgen Orasche: Data curation. Xun Zhang: Software. Josef Cyrys: Data curation, Writing review & editing. Bernhard Michalke: Data curation. Ralf Zimmermann: Investigation, Supervision. Jürgen Schnelle-Kreis: Data curation, Supervision, Writing review & editing.



Influence of New Year's fireworks on air quality – A case study from 2010 - 2021 in Augsburg, Germany

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Abstract

Fireworks have been shown to contribute short-term but potent source of ambient particulate matter (PM). Here we present a source apportionment-based approach to estimate the quantitative contributions of fireworks in releasing black carbon (eBC), polycyclic aromatic hydrocarbons (PAHs) and metals into urban ambient air on six New Year's Day fireworks events from the period 2010 to 2021. Simplified PMF analyses were performed to assign PAHs, eBCs, and metals to major contributors (building heating, traffic, and fireworks) of ambient PM. The trends of PM_{10} and $PM_{2.5}$ concentrations clearly showed the drastic increase of the concentrations on New Year's Days. The PMF analyses showed that, on average, about 35% (20-80% for individual years) of the PAHs and about 45% of eBC (10-100%) were associated with the fireworks. Metals presented in high concentrations in pyrotechnic sets, namely Ba, Cu, K, Mg, and Sr were attributed to fireworks about 90%, while Al was attributed to fireworks by 86%. Other metals (Ca, Cr, Fe, Na, Pb, Ti, and Zn) were attributed to fireworks by variable proportions averaging at 67%, 77%, 44%, 59%,

64%, 75%, and 33%, respectively. Overall, these findings complement future monitoring programs and regulations for fireworks emissions.

Keywords: Fireworks, Source apportionment, PAHs, eBC, Metals

1. Introduction

New Year's Day is internationally celebrated by releasing large quantities and a wide diversity of fireworks. People in many places simultaneously set off fireworks starting from midnight on December 31. Consequently, large quantities of particulate matter are released within a short period. According to a recent calculation by the German Environment Agency (Umweltbundesamt, UBA), the New Year's Eve fireworks emitted around 1,500 tons of particulate matter (PM_{10}) across Germany within a few hours (FEA, 2020). Since the vast majority of the fireworks used are ignited near the ground, this causes a sharp increase in the concentration of particulate matter in the air. Evaluations of the data from the German air quality measurement networks regularly show peak particulate matter concentration during New Year's Day with maximum hourly values around 1,000 $\mu g/m^3$ PM_{10}. A recent study on fireworks' emissions concluded that about 80% of the particulate matter emitted by the explosive content of the fireworks is in the $PM_{2.5}$ fraction, i.e., respirable (Keller and Schragen, 2021).

The links between air pollution from fireworks emissions and human health have been poorly studied. A study from the Netherlands examining the associations between PM_{10} concentrations and daily mortality in the period around New Year's celebrations from 1995-2012 did not reach a clear conclusion. In the study, linear regression models showed no clear association between PM_{10} concentrations and daily mortality, while case-crossover analyses suggested an association (Greven *et al*., 2019). Saucy *et al*. (2021) found an increased of cardiovascular mortality risk on fireworks days independent from NO_2 and $PM_{2.5}$ concentrations. A recent study on the toxicity of fireworks particles showed significant increases in reactive oxygen species (ROS) formation as a function of particles composition. They found that the high concentrations of Pb and Cu in some fireworks were responsible for the significantly increased toxicity compared to typical urban fine dust (Hickey *et al*., 2020).

Depending on the type, 25-40% of the fireworks used consist of pyrotechnic compositions. These are mostly black powder (a mixture of potassium nitrate, charcoal, and sulfur), that give bangs, whistles, and colors. Among other components, the metals used for coloring the fireworks (e.g., red: Sr and Ca, green: Ba and Cu, blue: Cu, white or silver: Mg, Al, and Ti, and gold: Fe) are released in large quantities during firework's set off. The contribution of fireworks in elevating the concentrations of many metals and sulfate on New Year's Day has been confirmed in

numerous studies in several countries, such as Auckland, New Zeland, Manila, Philippines, Mexico City, Mexico, and Rotterdam, The Netherlands (Lorenzo *et al.*, 2021, Retama *et al.*, 2019, Rindelaub *et al.*, 2021, Ten Brink *et al.*, 2019). The clear data situation is mainly due to the mixture and partly source-specific metals emitted by fireworks (Croteau *et al.*, 2010, Keller and Schragen, 2021). The study situation is different for carbonaceous components and especially polycyclic aromatic hydrocarbons (PAHs). To our knowledge, there is very limited evidence about PAHs emission factors or profiles from fireworks. Betha and Balasubramanian (2014) reported that PAHs profiles for particle-bound PAHs in various sparklers showed high variability in emitted PAHs, making it difficult to determine or quantitatively estimate the contributions of fireworks to air pollution with PAHs. Therefore, different studies arrived at different assessments of the significance of the contribution of fireworks to particulate matter pollution with PAHs.

For example, Pongpiachan *et al.* (2017) found an increase >150% in total PAHs concentrations during the fireworks period in Bangkok, Thailand. Their analyses using binary PAH ratios, hierarchical cluster, and principal component analyses (PCA) indicated that both road traffic and fireworks were major sources of PAHs. In contrast, Sarkar *et al.* (2010) reported that fireworks were not major source of PAHs during Diwali fireworks. They indicated that PAHs were either not correlated or negatively correlated with firework metals (Na, K, Mg, Al, Ba, Sr), but positively correlated with industrial and vehicle specific markers (Zn, V, Ni, Cr, Cu; $R > 0.5$), suggesting their common origin. Shi *et al.* (2014) also found PAHs were not directly influenced by fireworks, but rather affected by biomass combustion (firework is made by paper and cracker). A recent study in the U.S. also showed no significant contribution of fireworks to PAH concentrations, although the diagnostic ratios used in the study indicated their contributions (Jia *et al*., 2020).

For Germany, however, there have been a few studies to date that have examined in more detail about the contributions of fireworks to pollutant levels beyond particulate matter mass concentrations. In this study, we aimed to investigate the contribution of fireworks to air pollution with selected pollutants, in particular PAHs, black carbon (BC) and metal elements in Augsburg, Germany. For this purpose, measurement and data analysis from six periods around the turn of the year from 2010 to 2021 were evaluated. Simplified positive matrix factorization (PMF) analyses were performed to estimate the contributions of the main pollutants to PAHs, BC, and metals. This approach made it possible to estimate the contributions of fireworks to particulate pollution with an estimated uncertainty of about 50%. Furthermore, the special situation at the New Year 2020/21 allowed investigating the effects of significantly reduced fireworks on air quality. Due to various regulations imposed in the context of the COVID-19 pandemic, including a

prohibition on the sale of fireworks, a ban on fireworks in public places, and a nighttime curfew, significantly reduce fireworks were set off in the city, especially in 2020/21.

2. Methods

2.1 Monitoring site location and study period

The sampling site was located on the campus of the University of Applied Sciences Augsburg (UAS, 48.35793 N, 10.91544 E), specifically at the ambient aerosol monitoring station operated jointly by the Helmholtz Zentrum München and the University of Augsburg. The site is characterized as an urban background site with 120 m away from the nearest road and ~250 m far from the nearest residential buildings. A more detailed description of the corresponding location can be found in the previous publication (Gu *et al.*, 2011). In this study, particulate matter measurements are analyzed biennially from December 24 till January 7 at the turn of years 2010-2011, 2012-2013, 2014-2015, 2016-2017, 2018-2019 and 2020-2021.

2.2 Continuous measurements and particle sampling

The Tapered Element Oscillating Microbalances (TEOM, model 1405-F, Thermo Fisher Scientific Inc., U.S.) was used to measure particle mass concentration of PM_{10} and $PM_{2.5}$. Equivalent black carbon (eBC) was determined by aethalometers (Magee, model AE31 until 2019 and AE33 since 2020, Aerosol d. o. o., Slovenia). Measurement values of air pollutants were evaluated based on their hourly averages. In addition, hourly averages of meteorological parameters including wind speed (WS), wind direction (WD), temperature (T), and relative humidity (RH), measured at the UAS site. Moreover, precipitation data collected from the German Weather Service (Deutscher Wetterdienst, DWD), were considered for the interpretation of the results.

$PM_{2.5}$ samples were collected from a sequential filter sampler (Partisol 2025, Thermo Scientific, USA). Daily $PM_{2.5}$ samples (midnight to midnight) were collected on quartz fibre filters (QFF: T293, Munktell, Grycksbo, Sweden), heated at 500 □ overnight before analysis. Samples were returned to the laboratory on a weekly basis, packed in Petri dishes, and stored at -20 □ until chemical analysis. One blank sample was collected every week as a control. In total, 79 $PM_{2.5}$ samples were collected and investigated within this study.

2.3 Chemical analysis of $PM_{2.5}$ samples

The organic components and elements were analyzed using sub-samples of the original QFF. The organic composition of the $PM_{2.5}$ samples was determined using *in situ* Derivatization Thermal Desorption Gas Chromatography Time-of-Flight Mass Spectrometry (DTD-GC-TOF-MS) method (Schnelle-Kreis *et al.*, 2011). A

total of 13 PAHs, including fluoranthene (Flu), pyrene (Pyr), Benzo[a]anthracene (BaA), Chrysene (Chr), the sum of Benzofluoranthenes (BbjkF), Benz[e]pyrene (BeP), Benz[a]pyrene (BaP), Indeno[1,2,3-cd]pyrene (Ind), Dibenz[ah]anthracen (DahA), Benmzo[ghi]perylene (BghiP), Coronen (Cor), and Retene (Ret) (Table S1), were quantified. In addition, the concentrations of two oxidized aromatic compounds, 1,8-Naphthalic anhydride (NA) and 4-H-Cyclopenta[def]phenanthren-4-one (CPO) and 6 Hopanes (17ß(H),21a(H)-30-Norhopane (29aß), 17ß(H),21a(H)-30-Norhopane (29ßa), 17a(H),21ß(H)-Hopane (30aß), 17ß(H),21a(H)-Hopane (30ßa), 17a(H),21ß(H)-Homohopane (31aßS), and 17a(H),21ß(H)-Homohopane (31aßR)) were evaluated. Subsequently, 27 elements, namely Al, As, B, Ba, Be, Ca, Cd, Co, Cr, Cu, Fe, K, Li, Mg, Mo, Na, Ni, P, Pb, S, Sb, Se, Sn, Sr, Ti, V, and Zn were evaluated by Inductively Coupled Plasma-Mass Spectrometry (ICP-MS) using rhodium and lutetium as internal standards (Gu *et al.*, 2011). The limits of quantification (LOQ) of the methods (GC-MS and ICP-MS) were added in the supporting information (Table S1). For the quality assurance/quality control (QA/QC), the method is based on a internal calibration, which means that an isotopically labelled standard mixture is added to each calibration point as well as to all samples. The quality of the measurements is ensured by frequent measurements of reference samples and weekly replicates of real samples (Orasche *et al*., 2011).

2.4 PMF analysis

In recent years, positive matrix factorization (PMF) (Paatero and Tapper, 1994) has been widely used in sources apportionment studies. Unlike most source apportionment studies conducted to date, our PMF analysis aims neither to identify all possible sources of $PM_{2.5}$ nor estimate their contributions to the measured $PM_{2.5}$ values. Rather, the goal was to estimate the contributions of fireworks emissions to the PAHs, eBC and metal elements concentrations. Therefore, we focused on the source groups that have already been shown to be the major contributors of PAHs and elemental carbon (EC) in previous studies in Augsburg (Gu *et al.*, 2013). By limiting the analysis to the main contributors to PAHs and BC, the contribution of the sources identified in our study to the $PM_{2.5}$ concentration is certainly overestimated, as important contributions such as secondary inorganic aerosols are not considered. Previous studies have shown that fraction of ammonium nitrate and sulfate in urban background PM in Augsburg can average about 50% of the total particle mass in winter (Gu *et al.*, 2013).

However, from the contributions of PAHs, eBC, and metals to the factors determined by PMF and the proportional contribution of the fireworks factor to the $PM_{2.5}$ load on New Year's Day, the contribution of fireworks to the total load of PAHs, eBCs, and metals can be estimated with a reasonable degree of accuracy. A detailed description of the PMF

141 analysis can be found in the supporting information (SI, section 1).

142 **2.5 Toxic and mutagenic equivalent factors of PAH**

143 The carcinogenic risk of a PAH mixture is often expressed by its BaP equivalent concentration (BaP_{TEQ}) (Han,
144 2011). To normalize the toxicity of different PAHs in $PM_{2.5}$, it was calculated using the equivalent mass concentration
145 based on BaP and the value of toxic equivalency factors (TEFs) (Table S2), which has been described elsewhere (Liu
146 *et al*., 2019). Similarly, BaP related mutagenicity (BaP_{MEQ}) was calculated, except that the TEF was replaced by MEF
147 (mutagenic equivalency factor). The BaP_{TEQ} and BaP_{MEQ} were calculated according to following equations (1-2):

148 $$\Sigma BaP_{TEQ} = \sum_{i=1}^{n} C_i \times TEF_i \quad (1), \quad \Sigma BaP_{MEQ} = \sum_{i=1}^{n} C_i \times MEF_i \quad (2),$$

149 where C_i=concentration of PAH congener *i*; TEF_i=the toxic equivalency factors (TEFs) of PAH congener *i*;
150 MEF_i=the mutagenic equivalency factors (MEFs) of PAH congener *i*. The toxicity assessment of PAHs was
151 determined by benzo(a)pyrene, as an equivalent for carcinogenicity (ΣBaP_{TEF}) and mutagenicity (ΣBaP_{MEF}).

152 **3. Results and discussion**

153 **3.1 Air pollutants trends around New Year's Days**

154 **3.1.1 Particulate matter**

155 The trends of PM_{10} (Figure S1) and $PM_{2.5}$ concentrations (Figure 1(a)) clearly showed the drastic increase of the
156 concentrations on New Year's Day. The data showed that there was massive increase in PM concentration at midnight.
157 However, a slighter increase was already observed in the hours before midnight. The temporal differences in reaching
158 the maximum concentrations were observed between 0:00 and 2:00, which for $PM_{2.5}$ ranged from about 60 (2020-
159 2021) to > 600 μg/m^3 (2012-2013). Possible causes underlying this condition were influenced by different intensity
160 of the fireworks and the dispersion conditions, especially wind speed. Normally, the extremely high particle
161 concentrations decline within a few hours, resulting in the concentrations below 25 μg/m^3 again on January 2. When
162 the concentration trends are considered across the entire interval, numerous periods of different length with sometime
163 significantly elevated $PM_{2.5}$ and PM_{10} concentrations can be identified. The period between Christmas and New Year's
164 Eve 2010 was particularly striking, with $PM_{2.5}$ concentrations exceeding 70 μg/m^3 in some periods. However, on
165 average, $PM_{2.5}$ and PM_{10} concentrations on New Year's Day were significantly higher than on the days before or after
166 (Figure 1(b)), which was consistent with previous study (Hamad *et al*., 2016).

167 **3.1.2 Black carbon**

168 A possible influence of the fireworks on the eBC concentration was not clearly detected on New Year's Day

(Figure 1(c)). However, a significant peak of eBC concentrations was found at most of the year changes, but it was much less pronounced than the peaks of PM concentration. It was also noticeable that the increase in concentration was significant before midnight in most years (Figure 1(d)). In addition, many short episodes with eBC concentrations above those of New Year's Day were observed in almost all years. As previously observed for $PM_{2.5}$, the period between Christmas and New Year's Eve 2010 was characterized by comparatively high eBC concentrations. However, on average the studied New Years, the average concentration of eBC on New Year's Day was significantly or highly significantly higher than on the days before or after, indicating that eBC concentrations may also be influenced by firework (Lin *et al.*, 2016). Despite the higher variability, the eBC concentration was strongly correlated with PM concentrations during the observation periods (BC *vs.* $PM_{2.5}$, 0.789; BC *vs.* PM_{10}, 0.843, $p<0.01$).

3.1.3 Elements

A total of 27 metal elements were quantified by ICP-MS. Of these, 15 elements (i.e., Al, B, Ba, Ca, Cr, Cu, Fe, K, Mg, Na, Pb, S, Sr, Ti, and Zn) were quantified, while 12 elements (i.e., As, Be, Cd, Co, Li, Mo, Ni, P, Sb, Se, Sn and V) were excluded from further evaluation because their concentrations were below the limits of detection in all $PM_{2.5}$ samples. Three different temporal characteristics can be considered for the elements (K, Pb, and Fe), which were discussed here as an example (Figure 1(e-j)), while temporal characteristics for other elements were supplemented in SI (Figure S2). Elements with highly abundant in the pyrotechnic sets of the fireworks (e.g., K, S) or that can be emitted in very high amounts due to their known use in coloring the fireworks (e.g., Al, Ba, Cu, Mg, Sr, Ti) had indeed very high peak concentrations on the New Year's days (Lorenzo *et al.*, 2021), as can be illustrated by K element (Figure 1(e)). Slightly elevated concentrations were observed as early as December 31. On January 2, the low concentrations were reached again as period before the fireworks. Apart from the pronounced peak around New Year's Day, there were either an absent of concentration peaks or relatively low peaks observed. The differences between the New Year's Day and the comparison periods were highly significant (Figure 1(f)). The second group of elements (Cr, Pb, and Zn), in addition to pronounced peak concentrations on New Year's Day, also exhibited other concentration peaks before and/or after the fireworks display in some cases (Figure 1(g)). Similar to the $PM_{2.5}$ and the eBC, lead and zinc (Figure S2) also exhibited elevated concentrations during the episode between Christmas and New Year's Eve 2010, and significantly higher concentrations on New Year's Day (Figure 1(h)). This is particularly noteworthy since the aboved mentioned heavy metals are not (anymore) allowed to be used for fireworks approved in Germany (EU Directive, 2013). The third group includes B, Ca, Fe and Na. The course of the concentrations of these elements showed high

variability around the studied turn of the year with no noticeable peaks on New Year's Day (Figure 1(i)). Accordingly, there were also no significant differences between fireworks and comparison periods in the concentrations averaged over all periods studied (Figure 1(j)).

3.1.4 PAHs

In total, the temporal trends of PAHs concentrations were comparable to those of some heavy metal group (Cr, Mn, Pb, and Zn) (Figure S3). However, the peak concentrations on New Year's Days were much less pronounced or absent in some of the studied periods (Figure 1(k)). More frequent and sometimes higher peak concentrations than on January 1 were observed during the comparison periods. When the highest PAHs concentrations occurred, the period between Christmas and New Year's Eve 2010 was particularly striking. Overall, slightly higher concentrations were detected on January 1 for all PAHs than in the comparison periods, but these were not significantly different (Figure 1(l)). However, it is worth mentioning that the PAHs concentrations were classified as high concentration in the observed periods. For example, the annual average of BaP concentration was 10 times higher than the EU target value of 1 ng/m^3 (Hellén *et al.*, 2017).

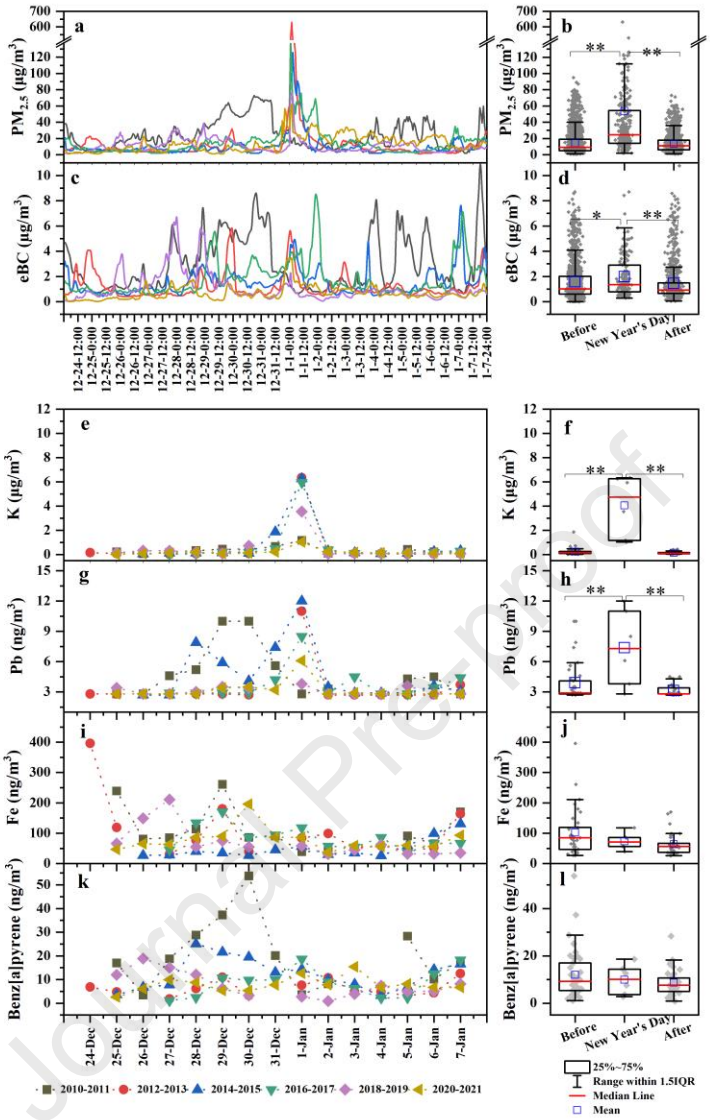

Figure 1. Left panel, Time series of the hourly mean concentrations of $PM_{2.5}$ (a) and eBC (c), and daily mean concentrations of K (e), Pb (g), Fe (i), and Benz[a]pyrene (BaP) (k) in the periods studied. Right panel, summarized comparison of the hourly means of the concentrations of $PM_{2.5}$ (b), eBC (d) and the daily means of the concentrations of K (f), Pb (h), Fe (j), and BaP (l) on New Year's Day with the reference periods before and after. The significance levels (**, $p<0.01$, *, $p<0.05$) refer to the differences between the respective means.

3.2 Meteorological impacts on $PM_{2.5}$ and eBC concentrations

Under different meteorological conditions, the concentration of pollutants on the ground from the same source can vary by tens or even hundreds of times due to atmospheric dispersion. Therefore, the Spearman correlation coefficients (r) were calculated between the air pollutants concentrations and meteorological variables in the observed

periods. Our analysis revealed that the air pollutants concentrations were negatively correlated with wind speed (WS) and temperature (T) and positively correlated with relative humidity (RH) (Table S3), indicating the temporal variability of PM concentrations were strongly influenced by meteorological variables. However, meteorological conditions alone did not provide a discernible approach to explain the sometimes very large differences in $PM_{2.5}$ and eBC concentrations on New Year's Day.

The period around the turn of 2010-2011 had several notable features. First, there was a multi-day episode with high PM concentrations from the afternoon of December 28 to the morning of New Year's Eve. This period was characterized by low average WS (< 1.5 m/s) and relatively constant high RH (Figure S4). During the period between January 3 and 6, comparatively high concentrations were observed at night, each associated with low WS and high RH, which decreased significantly during the respective day simultaneously with increasing WS and decreasing RH. During these two periods, the highest concentrations were associated with circulating winds with a slight northeasterly component (Figure S4e). However, the absence of high concentrations on New Year's Day, which could be attributed to fireworks, was particularly noticeable at the turn of the year 2010-2011. This was also confirmed for most of the metals analyzed. Only the metals considered characteristic of fireworks (Al, Ba, Cu, K, Mg, Sr, Ti) showed elevated concentrations (Figure S2). Neither dispersion conditions prevailing on this day, wind with low velocities from south-west, nor precipitation offered a plausible explanation for this finding. Precipitation was observed only at the beginning and the end of the 14 days period. Only individual concentration peaks were found around the turn of the year 2012-2013 (Figure S5a). These occurred in each case at night during low WS and high RH as already described for 2011. The $PM_{2.5}$ peak concentration on New Year's Day was very pronounced and associated with similar meteorological conditions as on New Year's Day 2011 (and 2019), i.e. low winds from south-west (Figure S4f and S8f). Thus, just as meteorological conditions failed to explain the missing PM peak on New Year's Day 2011, our available data also failed to explain the exceptionally high $PM_{2.5}$ concentration on January 1 2013. The situation at the turn of 2014-2015 was very similar to that of 2012-2013. However, unlike the previously described period, phases of low WS and high RH also occurred in this study and were not associated with high PM concentrations (Figure S5 and S6). The high PM concentrations on New Year's Day are associated with WS below 1 m/s (Figure S5f and S6f).

New Year's Day 2017 occurred during a relatively long period with WS around or below 1 m/s, frequently changing WD and high RH with low T compared to the other periods (Figure S7). During this period, a gradual increase in eBC concentration was observed. However, no additional eBC peak occurred on New Year's Day. The

248 $PM_{2.5}$ concentration, on the other hand, exhibited the significant peak in concentration at midnight as expected for
249 New Year's Days. The period around New Year's Day 2018-2019 was very similar to the 2012-2013 period with high
250 PM concentrations at low WS and high RH, albeit much lower PM peaks were observed on New Year's Day (Figure
251 S8a). During the highest PM concentration, wind conditions were similar to 2013, with WS below 1 m/s from the
252 south-west. The situation around the turn of 2020-2021 was different from all previously periods (Figure S9). The
253 eBC concentration was comparatively low and did not show pronounced peaks, excluding the peaks on New Year's
254 Eve and New Year's Day. The $PM_{2.5}$ concentration exhibited almost identically high peaks on the late evening of New
255 Year's Eve and shortly after midnight on New Year's Day. However, unlike the previous New Year's Eve events, the
256 $PM_{2.5}$ concentration did not switch fell and declined slowly and fluctuated over several days. A direct connection
257 between the observed fluctuations and the meteorological parameters was not evident. However, it was noticeable that
258 the RH showed pronounced diurnal fluctuations in the days before the turn of the year, with mostly lowest values
259 around noon, while it was stable, at a relatively high level after the turn of the year.

260 In summary, the correlations between the meteorological parameters and the observed $PM_{2.5}$ and eBC
261 concentrations were statistically significant and provided clear contributions to the variability of the observed
262 concentration. However, meteorological conditions have not provided an identifiable method for explaining some of
263 the very large differences in $PM_{2.5}$ and eBC concentrations on New Year's Day.

264 **3.3 PMF Analysis**

265 The data were analyzed using PMF5.0 (EPA, US Environmental Protection Agency) to assign eBC, PAHs, and
266 metals to the most relevant sources. In this PMF analyses, PAHs, 15 elements, daily average of eBC and $PM_{2.5}$ (total
267 variable), and the some selected organic substances were included. Due to the small number of samples and limited
268 analyses (without inorganic ions), it was not possible to identify all sources relevant to the $PM_{2.5}$ mass. However, the
269 analytical data were sufficient to identify the major sources of PAHs, BC, and metals and to determine their relative
270 contribution of fireworks to these pollutants. Thus, the goal of PMF analysis was not to identify the entire contributors
271 to $PM_{2.5}$, but to identify the contributions of the major sources to the proportions of the above pollutants. As a result,
272 3 factors were separated and further described in more detail below. The corresponding factor profiles can be found
273 in the SI Figure S10.

274 **3.3.1 Factor profiles**

275 **Factor 1 - firework emissions**

Factor 1 was dominated by high concentrations of the elements: Cu (79%), Sr (79%), Ba (75%), Mg (71%), K (70%), Al (49%), and S (42%), which were strongly correlated with fireworks burning (Miranda *et al.*, 2004, Rai *et al.*, 2020). The chemistry of fireworks was commonly based on fuels and oxidizer, containing potassium nitrate (KNO_3), charcoal, sulfur (S). Al, Mg, strontium nitrate ($Sr(NO_3)_2$), and barium nitrate ($Ba(NO_3)_2$) were common compounds as effect charges of pyrotechnic products (Srinivasan, 2017, Keller and Schragen, 2021). When these compounds were burned, they emitted a distinctive flame color. Briefly, KNO_3 was commonly used as a propellant, while Al and Mg were used as fuels and white luminous agent in fireworks (Lorenzo *et al.*, 2021). In addition, the firework color was also formed by metal salts such as Sr for red, Ba for green, and Cu for blue-violet. These three elements were effective markers for fireworks (Walsh *et al.*, 2009, Vecchi *et al.*, 2008). Therefore, factor 1 was considered as "fireworks" emissions. On average, this factor also accounted for about 18% of the chromium, 12% of the lead and 2% of the zinc. Only about 2-4 % of the individual PAHs and about 5 % of the eBC were associated with this factor. Thus, PAHs in this factor, which can be interpreted as the average composition of fireworks emissions, have concentrations in the $PM_{2.5}$ between 6 and 280 µg/g. These values were comparable to the range of PAH concentrations in the emission PM reported in the previous study (Betha and Balasubramanian, 2014).

Factor 2 - domestic heating emissions

Factor 2 was characterized by high contribution of 1,8-Naphthalic anhydride (95%), PAHs (75-82%), 4-H-Cyclopenta[def]phenanthren-4-one (75%), eBC (73%), and hopanes (40-68%). 1,8-Naphthalic anhydride, and 4-H-Cyclopenta[def]phenanthren-4-one were oxidized polycyclic hydrocarbons (o-PAH) found in wood combustion emissions at high concentrations (Orasche *et al.*, 2012, Czech *et al.*, 2018), and therefore considered as a marker for wood combustion. In this factor, the hopane pattern showed high similarity with hopane pattern from coal combustion (Křůmal *et al.*, 2013). Therefore, in previous study in Augsburg, it was interpreted as indicator of exposure to brown coal combustion for domestic heating (Schnelle-Kreis *et al.*, 2007). Based on these results, factor 2 was interpreted as "domestic heating" emissions.

Factor 3 - traffic emissions.

Factor 3 was dominated by high concentrations of Ca (93%), Na (79%), Ti (66%), Zn (63%), Fe (54%), B (57%), Cr (56%), Pb (58%), Al (48%) elements, and 4 hopanes compounds (45%). Emissions from traffic were a significant source of metals to the atmosphere. These can come from the combustion of trace amounts in gasoline and diesel fuels, brake and tire wear particles, and resuspended road dust (Pant and Harrison, 2013, Sanderson *et al.*, 2014). Therefore,

the traffic emissions were divided into the following three categories: traffic exhaust, traffic abrasion, and traffic resuspension.

Ca and Zn were often added to lubricating oil to protect engine components (Liati *et al.*, 2015). Therefore, Ca and Zn have been considered as markers for traffic exhaust sources, specifically from diesel fuel (Sanderson *et al.,* 2014, Liati *et al.*, 2012). In addition, metal fragments (e.g., Fe- bearing) mechanically abraded from diverse parts of the engine and/or the exhaust after-treatment systems have also been found in the engines exhausts (Sappok *et al.*, 2012). In factor 3, the hopane pattern showed a high similarity to the vehicle exhausts pattern (Křůmal *et al.*, 2013). The class of traffic-related abrasion includes all particles that can be attributed to brakes and tires abrasion associated with motor vehicle and traffic emissions based on marker elements (e.g., Fe, Zn, Ti, and Cr) and morphology (Habre *et al.*, 2014, Pant and Harrison, 2013). For example, brake wear due to abrasive processes produced Fe, Ti, and Cr containing materials (Kukutschová and Filip, 2018). In addition, Zn has also been considered as a marker for tire abrasion, as it has been added to tire tread in the form of zinc oxide and organozinc compounds to facilitate the vulcanization process (Jandacka *et al.*, 2017). Resuspended material from traffic was primarily a mixture of fine material on the road and roadside that was stirred up by tire movement and headwinds. High concentrations of Na were most likely from salt based de-icing agent applied to Augsburg roads in winter (Gu *et al.*, 2011). Ti, Fe, and Al were considered as marker elements for mineral crustal particles such as suspended soil and road dust (Gu *et al*., 2011). Ca also probably originated from the resuspension of dust (Loyola *et al.*, 2012). In addition, Fe and Al were also identified as the marker elements for asphalt, along with small proportions of Cr and Zn (Mummullage *et al.*, 2016). Meanwhile, Cr and Pb in road dust could be derived from road paint ($PbCrO_4$) (Li *et al*., 2019). Thus, factor 3 can be summarized as "traffic" emissions. On average overall investigated periods, this factor contributed to about 14-21% of PAHs concentrations and 22% of eBC.

3.3.2 Factor contributions

As mentioned above, PMF explained the $PM_{2.5}$ concentrations reasonably well. However, a deeper analysis showed that some huge values (> 25 $\mu g/m^3$), such as the repeatedly discussed period between Christmas and New Year's Eve 2010, but also the very high value on New Year's Day 2013, were not captured in a representative fashion (Figure 1a). Figure 2 showed that the time series of the three factors' contributions and their respective average concentrations on New Year's Day and in the reference periods were recorded. Factor 1 (fireworks emissions) showed a significant peak in concentration on all New Year's Days. Small contributions of this factor to $PM_{2.5}$ were also

observed on New Year's Eve and partially on January 2. On the other days of the reference periods, factor 1 did not contribute to $PM_{2.5}$. Accordingly, the difference in concentrations between January 1 and the reference periods was highly significant (Figure 2b). Factor 2 (residential heating emissions) showed comparatively low concentration variations without pronounced peaks in all periods around the turn of the year (Figure 2c). However, the episode with comparatively high contribution of this source to $PM_{2.5}$ between Christmas and New Year's Day 2010 was striking. This has been already noted for $PM_{2.5}$, eBC, PAHs, and some elements. In addition, very low levels of this factor were found in the beginning of 2019. The comparison of all measured values showed no significant differences between New Year's Day and comparison periods (Figure 2d). Like factor 2, factor 3 (traffic emissions) showed a little variations in concentration (Figure 2e). The episode in 2010 described for factor 2 did not occur here. However, it was noticeable that in some years, very low concentrations of this factor were estimated for January 1. To our knowledge, this was an artifact of the PMF analysis, which was not able to fully separate factor 1 from factor 3. As a result, lower concentrations of these factors were found on New Year's Days than in the comparison periods.

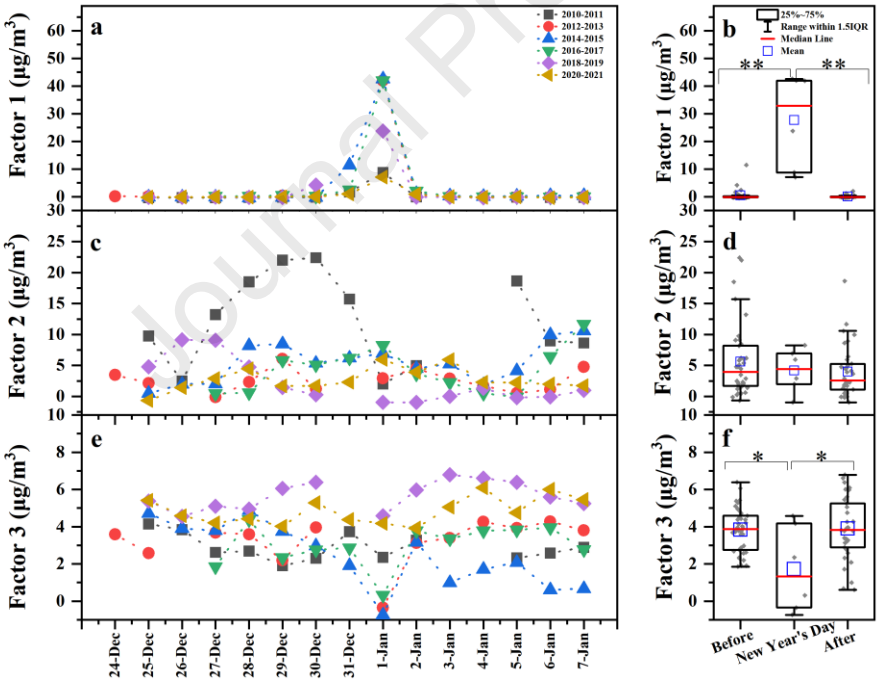

Figure 2. Left panel, Time series of the daily contributions of the source factors to the $PM_{2.5}$ concentration*. Daily mean concentrations of factor 1 (a) factor 2 (c) and factor 3 (e) in the periods studied. Right panel, Summarized comparison of the daily means of the concentrations of factor 1 (b), 2 (d) and 3 (f) on New Year's Day with the reference periods before and after. The significance levels (**, $p<0.01$, *, $p<0.05$) refer to the differences between the respective means.

Note: the absolute concentrations of the three factors were overestimated because many $PM_{2.5}$ sources were not considered such as, secondary organic aerosols.

3.3.3 Proportion of fireworks in particulate PAHs, eBC, and metals on New Year's Days

Based on PMF analysis, the contributions of fireworks to air pollution with PAHs, eBCs, and metals on New Year's Day can be estimated. The basis for the estimation were the average concentrations of the respective component and $PM_{2.5}$ estimated from PMF analysis in factor 1 (fireworks emissions) and the contribution of factor 1 to $PM_{2.5}$ on the New Year's Days.

On average overall periods investigated and all quantified PAHs, fireworks accounted for about 35% of the PAHs. Thereby, there were large differences between the individual New Year's Days. For instance, the lowest contribution from fireworks was estimated for January 1, 2021, with an average PAHs contribution of 6%. However, on New Year's Day 2019, about 84% of PAHs were associated with the fireworks emissions. On New Year's Day 2011, 2013, 2015, and 2017, fireworks contributed an average of 20%, 56%, 28%, and 24% of PAHs in $PM_{2.5}$, respectively. The ranking of fireworks contributions to eBC concentrations was analogous to that of PAHs. The lowest contribution was found about 12% on New Year's Day 2021, while the 2019 eBC (calculated) could be entirely from this source. For 2011, 2013, 2015, and 2017, the contribution of fireworks in the total eBC load was estimated as 26%, 64%, 42%, and 26%, respectively. On average overall periods studied, the contribution of fireworks to eBC was about 45%. As expected, the pattern of metals contributions from fireworks consisted of two parts. Firstly, the metals (and sulfur) present high concentrations in the pyrotechnic sets and have no very strong source on the fireworks days, i.e., Ba, Cu, K, Mg, S, and Sr were attributed to the fireworks by more than 91% on average. Al is attributed to fireworks by about 86%, which further supported by previous study (Lorenzo *et al*., 2021). It was also found that some firework tracer species (Cu, Ba, Sr, Al, and Pb), which exhibited the highest enrichments during the fireworks display. Only small variations in the proportions from year to year were estimated. Thus, the very high concentrations of these substances on New Year's Days were almost entirely due to fireworks. Secondly, the metals that have strong sources besides fireworks had varying proportions due to fireworks on New Year's Days. On average for all New Year's Days studied, the proportions attributable to fireworks were estimated to be 67%, 77%, 44%, 59%, 64%, 75%, and 33% for Ca, Cr, Fe, Na, Pb, Ti, and Zn, respectively. As for PAHs, the lowest contribution of these elements from fireworks was determined to be 20% on average on January 1, 2021. In other years, the contribution of fireworks to these metals was quite variable.

In summary, it was possible to estimate the contributions of fireworks to air pollution with PAHs, eBC, and metals using PMF analysis. In contrast to previous studies, comparatively high contributions to PAHs concentrations were found on New Year's Days. The study also showed that the contributions from fireworks on New Year's Day 2021 were much lower than in the other years. The measures imposed due to the COVID-19 pandemic (ban on sale of fireworks, ban on fireworks in public places, and nighttime curfew) have caused a significant reduction in the intensity and duration of fireworks on January 1, 2021, leading to the observed reduction in emissions.

3.3.4 Limitations

PMF analysis developed in this study to estimate the contributions of fireworks to $PM_{2.5}$ on New Year's Days was adopted based on number of underlying hypotheses and therefore imposing limitations on the reliability of the expected results. The key hypotheses, their limitations, and the resulting uncertainties were briefly summarized below.

A condition for conducting PMF is a sufficient relationship between observations and variables. There are no clear guidelines for this in the literature. In our case, the ratio is about 2 (78 observations, 37 variables), which gives stable results of the PMF analysis. As our analysis showed, the PMF is able to detect singular events (here the fireworks), if they show significantly different source profiles compared to the other relevant sources. However, for obtaining stable PMF results it is advisable to combine several independent measurements of the events (fireworks). These can be observations at different times, as in our case, or observations at different locations at the same time.

Our PMF analysis was performed to estimate the contributions of fireworks to PAH and eBC concentrations. This assumes that the relevant sources for these substances can be identified. From our previous studies in Augsburg, traffic emissions and residential heating are known as the most important sources of PAHs and eBC (Li *et al*., 2018). We believed that the misclassification of PAHs and eBC from sources other than traffic and residential heating to the fireworks was negligible. An additional essential assumption of PMF analyses was that the profiles (composition) of the sources were constant during the period considered. However, due to changes in technology and legislation in the investigated period, i.e., traffic and residential heating, have changed in quantity and quality (composition). In addition to the introduction of particulate filters and the continuous tightening of emission standards, especially for diesel vehicle, the introduction of Augsburg Environmental Zone has certainly contributed to a qualitative change in traffic emissions. With the respective regulations (1. BImSchV, 2010) revision, the building heating sector will also shift to lower-emission fireplaces and therefore may also change the emissions quality. However, in general, we estimated that the changes in the emission profiles have small error in the analysis of the distribution of PAHs and eBC.

When discussing the results of PMF analyses, it was often assumed that the factors can be fully separated from each other. However, a closer look at the results shows that these were only the case if the profiles of the factors (composition) and their time courses differ significantly. The fireworks factor, by its nature, showed a clearly discernible pattern with distinct peaks on New Year's Days and small contributions on December 31 and January 2. On the other days of the comparison periods, this factor was closely zero. On the other hand, contributions from building heating on January 1, 2019, and contributions from transportation on New Year's days in 2013, 2015, and 2017 could not be determined. This resulted in an overestimation of the contributions from the other sources on these days. The extent to which these contributions were due to fireworks on the days in question cannot be clearly assessed from the available data. Conservatively estimated, we assumed an overestimation of the fireworks on these days of a maximum of 50% of the estimated value.

3.4 Carcinogenic and mutagenic potencies of PAHs

The application of carcinogenic equivalents (BaP_{TEQ}), and mutagenic equivalents (BaP_{MEQ}) to polycyclic aromatic hydrocarbons (PAH) concentrations can provide a more accurate risk assessment from environmental exposure to PAH. Several studies have adopted this application to assess the health risk of PAH (Liu *et al.*, 2019, Nadali *et al.*, 2021, Callén *et al.*, 2014).

Therefore, in this study, the BaP_{TEQ} and BaP_{MEQ} values were also calculated using the TEF and MEF lists (Table S2). The higher carcinogenic risks of total PAHs (ΣBaP_{TEQ}) were found in Augsburg New Year's days period with average values of 14.43 ± 4.67 ng/m^3 (Figure S11), which were higher than the target annual mean values of ΣBaP_{TEQ} range (0.7- 1.3 ng/m^3) in European countries (Ballesta *et al.*, 1999). In addition, the average concentrations of ΣBaP_{MEQ} (mutagenic potencies) were approximately of 18.83 ± 6.08 ng/m^3 (Figure S11), which were higher than those at the Italian residential zone (4.2 ± 2.7 ng/m^3 for $PM_{2.5}$) (Masiol *et al.*, 2012). And the BaP_{TEQ} and BaP_{MEQ} levels were higher during New Year's Day than whole period. The results indicated that many toxic compounds were threatening human health in the New Year's Day. However, it should be noted that the average data in this study were only collected over the 15 days (Dec.24-Jan.07), thus the level of carcinogenic and mutagenic potencies of PAHs may not fully represent the whole year in some extent.

4 Conclusion

Simplified PMF analyses were successfully used to assign PAHs, eBCs, and metals to their sources. The approach adopted did not aim to identify all possible sources, but was limited to separating the main contributors already

identified in previous studies. The emphasis was placed on clearly separating fireworks events. PMF analyses was possible to estimate how high the contribution of fireworks to air pollution with PAHs, eBC, and metals was on individual New Year's days. In contrast previous studies, that did not show the clear accusations between fireworks and PAH and eBC concentrations, our finding suggested that the PAHs and BC, although not a major source of fireworks, were still indirectly affected by biomass combustion associated with fireworks. However, the ΣBaP_{TEQ} and ΣBaP_{MEQ} levels were higher during New Year's Days period, suggesting that many toxic compounds threatened public health during New Year's Days period. Taken together, these findings call for future monitoring programs and regulations for fireworks emissions.

CRediT authorship contribution statement

Mohamed Khedr: Data curation, Methodology, Writing original draft. Xiansheng Liu: Data curation, Methodology, Software, Writing original draft. Hadiatullah Hadiatullah: Methodology, Software, Writing original draft. Jürgen Orasche: Data curation. Xun Zhang: Software. Josef Cyrys: Data curation, Writing review & editing. Bernhard Michalke: Data curation. Ralf Zimmermann: Investigation, Supervision. Jürgen Schnelle-Kreis: Data curation, Supervision, Writing review & editing.

Declaration of Competing Interest

The authors declare no conflicts of interest.

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Appendix A. supporting information

Additional details about the text, 12 figures (Figure S1-S12) and 2 tables (Table S1-S2) with detailed information on PMF analysis, health risk assessment, and meteorological factors influence on air pollution during New Year's day.

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Highlights

1. PMF analysis used to estimate the contribution of fireworks on New Year's Days.
2. About 35% of the PAHs and 45% of eBC were associated with the fireworks.
3. About 90% metals were associated with pyrotechnic sets of firework.
4. Our findings complement future monitoring programs for fireworks emissions.

Declaration of interests

☒ 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.

☐The authors declare the following financial interests/personal relationships which may be considered as potential competing interests: