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Source differences in the components and cytotoxicity of $PM_{2.5}$ from automobile exhaust, coal combustion, and biomass burning contributing to urban aerosol toxicity

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Abstract. The combustions of fuels, including oil, coal, and biomass, are main anthropogenic sources of atmospheric fine particulate matters ($PM_{2.5}$), however, their discrepant contributions to health toxicity risks of mixed ambient aerosol pollution dominated by respective emission intensity and chemical compositions are still unclear. In order to explore the quantitative differences of these combustion emissions, ten typical types of each source $PM_{2.5}$, i.e., vehicle exhaust, coal combustion, and biomass burning, were collected by laboratory simulated combustion and dilution channel sampler. Totally thirty type combustion samples were compared with monthly urban air $PM_{2.5}$ samples, which chemical characteristics and biological effects were investigated by component analysis and *in vitro* toxicity assays of human lung epithelial cells (A549). Heavy metals are more plentiful in $PM_{2.5}$ from coal combustion and automobile exhaust, while carbonaceous fraction was plenteous in biomass burning. The overall cytotoxicity of $PM_{2.5}$ was automobile exhaust > coal combustion > biomass burning, with different toxicity pathways and triggers. The toxicity of $PM_{2.5}$ from gasoline/diesel and biomass combustion was relevant to the combination of carbonaceous and water-soluble components, but the toxicogenic capacity of coal combustion $PM_{2.5}$ was mainly related to the high content of heavy metals. All these three emission categories of anthropogenic combustion sources were more toxic than ambient $PM_{2.5}$ and should be the main independent contributors to the cytotoxicity of mixed urban air $PM_{2.5}$. Associated with the source apportionment results of positive matrix factorization (PMF) model that automobile exhaust, coal and biomass combustion contributed 27.7%, 25.2% and 13.1% of ambient air $PM_{2.5}$, respectively, the toxicological results suggest automobile exhaust and coal combustion are priority emissions with higher toxic pollutants to be reduced preferentially for precise urban $PM_{2.5}$ pollution control ensuring public health safety.

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1 Introduction

As a mixture of multiple sources, ambient particulate matters (PMs) arise from anthropogenic activities are continuously deteriorating the urban air quality, particularly in developing countries. Among these, fine PMs with an aerodynamic diameter of less than 2.5 μm ($PM_{2.5}$) is recognized as a serious public health concern due to its long persistence in air, carcinogenicity and acute toxicity to humans (Al-Kindi et al., 2020). There were extensive epidemiological evidences that airborne PM_s can cause serious negative effects on human health, such as cardiovascular diseases, respiratory diseases, genetic mutations, and developmental disorders (Chowdhury et al., 2022;Lelieveld et al., 2021;Smith, 2021;Clemens et al., 2017). Besides natural sources like dust and sea spray, the vast majority of aerosols come from anthropogenic activities such as energy consumptions, including the combustion of fossil fuels causing industrial emissions and automobile exhaust, and biomass burning (McDuffie et al., 2021;Wu et al., 2022). Finally, these diverse sources make the ambient air $PM_{2.5}$ become a complex mixture with multiple chemical components varying with time and space, which consisting mainly of sulfate, nitrate, ammonium, organic carbon (OC), elemental carbon (EC), mineral and trace metals (Bari and Kindzierski, 2016). However, which specific components and which particular sources are the most critical factors dominating the aerosols' health risks, still leave puzzles unsolved.

Past studies performed in various countries have focused on physicochemical characterization or biological effects of ambient air $PM_{2.5}$ respectively (Weagle et al., 2018;Jia et al., 2017;Wang et al., 2020). For example, the source analysis of $PM_{2.5}$ by photochemical modeling (Bao et al., 2018), chemical composition of regional $PM_{2.5}$ (Chi et al., 2022), and the mechanism of $PM_{2.5}$ toxicity was independently reported recently (Jia et al., 2020). Because differences in particle composition, sources, and toxicity appear in different urban environments (Zhao et al., 2019;Wang et al., 2022a), the source profiles of different emission inventories were applied to elucidate aerosol pollution characteristics and control strategies. For instance, it was found that straw burning during the harvest season is a major trigger of severe air pollution in many regions (Sahu et al., 2021). Aerosols from open biomass burning in the Amazon had a stronger ability to induce reactive organic species (ROS) than laboratory-generated secondary organic aerosols (Tuet et al., 2019). The particle composition of motor vehicle exhaust was related to automobile types with various fuels, engines, and loads (Lin et al., 2020). A strong catalytic reactivity of metals in PMs emitted from diesel vehicles was observed by dithiothreitol (DTT) assay (Jesus et al., 2018). Sulfate is a major component of PMs from Xi'an city, western China, mainly released from residential coal combustion activities (Dai et al., 2019). SMK-1 is an important signal pathway in the toxicogenic mechanism of $PM_{2.5}$ from coal combustions (Sun et al., 2020). Although there were emerging studies on particle emissions from single sources, quantificationally comparative studies on multi-source pollutants as well as the composition and toxicity of various sources are still limited. Furthermore, there is a particular lack of understanding regarding the relative contribution of each specific source to ambient aerosol pollution risks considering their different components' roles.

The main objective of current study was to compare the chemical components and corresponding toxicological effects of various representative anthropogenic combustion sources and their contributions to ambient aerosol health risks. The aim is to provide detailed guidance on the targeting and precise control of sources with prominent risks based on their pivotal toxic

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components. Therefore, we collected both ambient $PM_{2.5}$ samples from urban air and abundant representative source $PM_{2.5}$ samples from automobile exhaust, coal combustion, and biomass burning. Their profiles of chemical compositions and *in vitro* cytotoxicity were investigated and intercompared, to assess the differences in source-to-receptor toxicity and to infer the core toxicogenic components and respective harmful contribution. The pivotal toxicogenic components were identified based on the source-sink bi-directional composition-effect results, which were further used to assess the health toxicity contribution of various emission sources to atmospheric $PM_{2.5}$, supported by its source apportionment through positive matrix factorization (PMF) model. This study could advance the understanding to quantify the complex source contribution to high-risk $PM_{2.5}$ emission oriented to public health, which is imperative for precise prevention and control of atmospheric PMs pollution.

2 Materials and methods

2.1 Collection of $PM_{2.5}$ samples directly from anthropogenic emissions of 30 typical combustion sources and monthly urban air

As the main anthropogenic sources of the ambient air $PM_{2.5}$ pollution, totally 30 types of $PM_{2.5}$ samples emitted directly from automobile exhaust, coal combustion, and biomass burning were respectively collected as follows for both chemical and toxicological analyses.

Based on the classification of automobile fuel types as well as load and tailpipe emission standards provided by the 2019 Annual Report on Environmental Management of Mobile Sources in China, a total of 10 types of vehicles were chosen for exhaust investigation. They were further categorized into 7 sub-groups, including small duty gasoline coaches (SDGCs), small duty diesel coaches (SDDCs), middle duty diesel coaches (MDDCs), big duty diesel coaches (BDDCs), light duty diesel vans (LDDVs), middle duty diesel vans (MDDVs), and heavy duty diesel vans (HDDVs). The detailed information of these representative local automobiles were showed in Table S1.

To cover all coal types consumed in the city, 10 representative types of coal were gathered for investigation. They were further grouped into 4 sub-groups, including 2 types of honeycomb coal (HC), 3 types of anthracite coal (AC) and 2 types of bituminous coal (BC) mainly for restaurant or household use, and 3 types of industrial coal (IC) for coal-fired power plants and steel-smelting industry. The detailed characteristic analysis of these typical coals purchased from local market were showed in Table S2.

Considering the biomass combustion in rural areas surrounding the megacity, 10 typical types of agricultural and forestry solid wastes were gathered for investigation. Because of the high annual production of three staple food crops (rice, wheat, and corn) as well as soybean, peanut and rapeseed, their straws generated after harvest are often used as fuels in rural households. In addition, woods were also common fuels. Therefore, straws of rice, wheat, corn, soybean, peanut, rape, and sesame, corncob, branches of peach and pine, were selected as biomass fuels and further divided into 2 sub-groups, including

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8 types of crop straw and 2 types of firewood. The detailed characteristic analysis of these representative biomass fuels collected from rural areas around Nanjing city were showed in Table S3.

$PM_{2.5}$ samples directly emitted from these combustion sources were collected by dilution channel sampling method (Figure S1), using a 4-channel particulate matter dilution sampler (HY-805, Hengyuan Technology Development Co., CN). Each sampling included 3 channels of quartz microfiber filter (Figure S2) and 1 channel of Teflon filter membrane with diameters of 47 mm, through a size selector for $PM_{2.5}$ with a flow rate of 160 L min^{-1}. Clean air was pumped for 10 min before and after each sample was collected. The blank quartz and Teflon filters were baked by a muffle furnace at 500 °C for 3 h and at 60 °C for 4 h, respectively. After being equilibrated in a constant temperature and humidity chamber for 24 h, the filters were weighed. The sampled filters were stored in a refrigerator at -20 °C before analysis.

As the actual mixture of various source particles in real environment, totally 16 ambient air $PM_{2.5}$ samples covering a year monthly were collected from December 2019 to October 2020 in the urban site of Nanjing city, Yangtze River Delta of eastern China, using a high-volume air sampler. Detailed procedures and sample information were described in previous paper (Li et al., 2022), but the purpose of using these air samples in current study was to compare them with the specific source samples for evaluating the chemical and toxicological contributions of the anthropogenic combustion sources to environmental aerosols pollution.

2.2 Chemical composition analysis

All collected source and ambient $PM_{2.5}$ samples were conducted various component analysis. For the concentrations of heavy metals in particulates, samples were acid digested and determined by inductively coupled plasma optical emission spectrometry (ICP-OES; Optima8000, PerkinElmer), while some elements at lower concentrations were measured by ICP mass spectrometry (ICP-MS; NexIONTM300X, PerkinElmer). Blank filter, reagent blank, and reference material (NIST SRM 1648a, urban dust) were adopted for analytical quality control. Carbonaceous species (OC and EC) in $PM_{2.5}$ were determined using a DRI-2001A OC/EC (Atmoslytic Inc., Calabasas, CA, USA). For the concentrations of water-soluble ions (WSIs), the main cations (Na^+, K^+, Mg^{2+}, Ca^{2+}, NH_4^+) and anions (NO_3^-, SO_4^{2-}, Cl^-, F^-) in $PM_{2.5}$ were measured by ion chromatography (IC, Thermo Fisher Scientific, USA), using the Metrosep C6-150/4.0 column for cations and the Metrosep A Supp 5 150/4.0 column for anions, respectively.

2.3 Preparing $PM_{2.5}$ suspension for cell exposure

Totally 30 source and 16 ambient $PM_{2.5}$ samples were also performed cytotoxicity tests. In order to elute the particles completely from the quartz membranes, the $PM_{2.5}$-loaded sample filter was cut into small pieces, immerged in ultrapure water and extracted six times (30 min for each) in an ultrasonic bath at 0 °C. The extract was then suction filtered through a 2.6 μm pore-size nylon membrane to remove possible quartz fragments, and the bulk filtrate was freeze-dried back to pure $PM_{2.5}$ powder. Ultimately, based on particle mass, the gathered $PM_{2.5}$ was dispersed by sterile phosphate-buffered saline (PBS) to a

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concentration of 400 mg L^{-1}, and then diluted to $PM_{2.5}$ suspension of 80 mg L^{-1} with serum-free Dulbecco's modified eagle medium (DMEM) medium for following *in vitro* cell exposure (Li et al., 2022).

2.4 Cell culture and *in vitro* $PM_{2.5}$ exposure

The A549 human lung epithelial cells were cultured in RMPI-1640 medium (Gibco, USA) supplemented with 10% fetal bovine serum (FBS, Hyclone, USA) and 1% antibiotic penicillin-streptomycin (100 U mL^{-1}) at 37 °C in a 5% CO_2 incubator. Cell viability was assayed by methylthiazoletetrazolium (MTT) (Chen et al., 2019). After trypsin action, the density of cells in the logarithmic growth phase was adjusted to 1×10^5 mL^{-1}. Cell suspensions were inoculated into 96-well plates (Costar, USA) at 100 μL per well. The blank control well (without medium and $PM_{2.5}$ suspension) and reagent control well (with medium but without $PM_{2.5}$ suspension) were set together. After incubation for 24 h, various types of $PM_{2.5}$ suspension (80 mg L^{-1}) were added to 96-well plates and incubated for 24 h. Fresh medium and MTT reagent (Solarbio, Beijing, CN) were added to each well and the supernatant was discarded, then 100 μL of formazan lysate was added to each well. The optical density (OD) values were measured at 490 nm using a microplate reader (Thermo MULTISKAN FC, USA). Cell viability (%) = ($OD_{treatment}$ − $OD_{blank\ control}$) / ($OD_{reagent\ control}$ − $OD_{blank\ control}$). The oxidative stress (ROS) and inflammatory cytokines (TNF-α and IL-6) in the supernatant were analyzed by enzyme-linked immunosorbent assay (ELISA) kits (Jiangsu Enzyme Biotechnology Co., Ltd., CN), and OD values were measured at 450 nm (Huang et al., 2020;Pang et al., 2020).

2.5 Data analysis

The statistical analysis was performed by IBM SPSS statistics 24 and plotted by Origin 2020b software. Pearson correlation coefficients were produced by the correlation analysis. The variance was statistically significant when the statistical test level was $P < 0.05$, and extremely significant when $P < 0.01$.

The source apportionment of $PM_{2.5}$ mass in ambient air was conducted by the receptor model PMF (EPA PMF version 5.0). Major constituents (OC, EC, Cu, Cr, Co, Ni, As, Pb, Mn, V, Na^+, K^+, Mg^{2+}, Ca^{2+}, NH_4^+, Cl^-, F^-, NO_3^-, and SO_4^{2-}) were selected as input data, and a four-factor solution was chosen as the optimal solution based on an assessment of the interpretability of the source profiles and the seasonal variability of the source contributions.

3 Results

3.1 Contributions of combustion sources to urban ambient air $PM_{2.5}$

As shown in Figure S3, although have been significantly improved with the national air quality in recent years, the daily $PM_{2.5}$ concentrations of typical Nanjing city still exceeded the healthy guidelines obviously, with higher urban air $PM_{2.5}$ pollution level in the cold season[23]. Four major sources of the ambient $PM_{2.5}$ were produced by the PMF model, i.e., secondary aerosols, automobile exhaust, coal combustion, and biomass burning, which account for 34%, 27.7%, 25.2%, and 13.1% of total $PM_{2.5}$ mass concentration, respectively. Their source profiles and proportions were showed in Figure 1. Therefore, although the

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contribution of secondary aerosols cannot be ignored, the main anthropogenic sources of urban air $PM_{2.5}$ were primary emissions from the various fuel combustions.

3.2 Chemical compositions of $PM_{2.5}$ from 30 different emission sources and ambient air

Representative chemical components including carbonaceous fractions, heavy metals and WSIs of all $PM_{2.5}$ samples from both ambient urban air and 30 typical anthropogenic combustion sources (covering different categories of automobile exhaust, coal combustion, and biomass burning) were analyzed and compared with each other.

According to the comparison of $PM_{2.5}$ bound carbonaceous fractions (Figure 2), automobile and biomass sourced aerosols contained significantly higher total carbon (TC) content than coal combustion and ambient air, while the OC/EC ratio trend was ambient air > coal combustion > biomass burning > automobile exhaust sources. It indicated that the carbon content of ambient $PM_{2.5}$ mixture was lower and dominated by OC than that of anthropogenic combustion sources. Figure S4-S7 showed the detailed carbon fraction characteristics (contents and ratio) of $PM_{2.5}$ from each specific source. Carbonaceous fractions in automobile exhaust $PM_{2.5}$ were high but the difference between OC and EC content was small. Depending on the diverse automobile fuels, loads and tailpipe emission standards, the concentrations of carbon fractions in exhaust $PM_{2.5}$ varied widely with vehicle categories. The carbonaceous portion of $PM_{2.5}$ gradually declines as emission regulations rise, and EC likewise declines dramatically (Figure S4). However, such differences among coal types were less, except the bituminous coal with extreme high OC (Figure S5). The biomass combustions differed from plant species that tree branches generally contained higher carbon contents than crop straws (Figure S6).

Based on the grouped (Figure 3) and detailed (Figure S8-S11) distributions of the measured heavy metals in various $PM_{2.5}$, the V concentrations of combustion sources were generally higher while Co and Mn were lower than ambient urban air. Coal combustion emissions carried highest levels of Pb and were enriched in Cu and As (Figure S9), while biomass combustions were rich in Cr and Ni (Figure S10). However, automobile exhausts were enriched in most heavy metals, especially Cu, and Cr, Ni, V, Mn (Figure S8). Heavy metals from different types of automobile exhausts with the same emission standard varies greatly. Anthracite and industrial coal combustions contain similar heavy metals much more than bituminous coal. Generally, Pb, V, Mn, As, and Cu in branches were higher than straws, while Cr, Ni, and Co were dominant and higher in straw burning emissions. A special discovery was that corn cob burning $PM_{2.5}$ carried more heavy metals than corn straw and was the biomass with the highest emission levels of heavy metals. Correspondingly, ambient air $PM_{2.5}$ were also rich in most metals, especially Mn, Pb, and Ni, Cu, Cr. Therefore, coal combustion sources might contribute most Pb to urban ambient air, and contribute significant Cu and As with automobile exhaust emissions, while biomass burning and automobile sources contribute the Cr and Ni. Besides natural dust, automobile exhaust should be the main anthropogenic source of airborne Mn. Considering the PMF source apportionments of ambient aerosols, automobile exhaust should be the main source of Cr in urban air $PM_{2.5}$, and also the source for Cu together with coal combustion.

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According to the comparisons of water-soluble cation and anion concentrations in various $PM_{2.5}$ (Figure 4), coal combustions contained highest SO_4^{2-} and NH_4^+, automobile exhausts had highest contents of NO_3^-, and Na^+, Ca^{2+}, while biomass burning sources contained highest K^+ and Cl^-, but Mg^{2+} was the lowest for all sources. However, the urban ambient air $PM_{2.5}$ contained highest NO_3^- and were also dominated by SO_4^{2-} and NH_4^+, for which NO_3^- should be mainly contributed by secondary aerosols and automobile primary source, SO_4^{2-} and NH_4^+ should be significantly from coal combustions. Besides NO_3^-, Na^+ and Ca^{2+}, automobile source $PM_{2.5}$ also had the highest F^- and Mg^{2+} concentrations than other sources. The detailed concentration distributions of WSIs in $PM_{2.5}$ from each specific source were provided in the supplementary information (Fig S12-S14). The WSIs levels vary widely with specific source categories. LDDVS-2 had the lowest amount of WSIs compared to the other automobile exhausts (Figure S12). Similar to the metal composition, bituminous coal also had the lowest WSIs among all coals (Figure S13). Compared to branches, crop straws had much greater levels of K^+, Cl^-, SO_4^{2-} and less levels of F^-, NO_3^- (Figure S14).

To summarize, the overall concentrations of measured TC, cumulated heavy metals and WSIs in $PM_{2.5}$ from each source type were showed in Figure 5. Among all source emission and environmental receptor samples, the cumulated heavy metals from coal combustion was highest and automobile exhaust was higher than ambient $PM_{2.5}$, the overall carbon contents from automobile exhaust and biomass burning were both higher than ambient $PM_{2.5}$, while only the cumulated soluble ions in $PM_{2.5}$ from primary source of coal combustion was equivalent to the ambient aerosols. In a word, chemical compositions of $PM_{2.5}$ distributed much diversely and varied significantly with the specific source types of anthropogenic combustion emissions.

3.3 Cell viability, oxidative stress and inflammation levels exposed to various $PM_{2.5}$

After 24 h exposure to the same dose of different $PM_{2.5}$ obtained from specific emission sources, the A549 lung cells also showed varied toxicological responses (Figure 6). The survival rate of cells exposed to automobile exhaust $PM_{2.5}$ was much lower than ambient air $PM_{2.5}$ (Figure 6a). Automobile exhaust $PM_{2.5}$ induced the highest ROS production in cells higher than biomass burning and both sources were also much higher than ambient $PM_{2.5}$ (Figure 6b). Coal combustion induced the highest cellular IL-6 production followed by automobile exhaust that was also higher than ambient air $PM_{2.5}$, while the $PM_{2.5}$ from automobile exhaust and biomass burning induced similarly higher cellular production of TNF-α than ambient $PM_{2.5}$ (Figure 6c, d). These results suggested that, anthropogenic combustion emission $PM_{2.5}$ had stronger ability to induce oxidative stress and inflammatory injury in cells than ambient air $PM_{2.5}$, thus resulted in the higher probability of apoptosis induction. Generally, the $PM_{2.5}$ from primary source of automobile exhaust posed the strongest overall toxicity. Therefore, to protect public health by controlling $PM_{2.5}$ pollution, the anthropogenic combustions were key target sources, especially the most toxic automobile $PM_{2.5}$ should be reduced preferentially.

3.4 Correlations between various $PM_{2.5}$ components and toxicity endpoints

Pearson correlation coefficients between chemical compositions and cellular toxicological response indicators were applied to screen the key components of all $PM_{2.5}$ involved in cell injury (Figure 7). It was found that, the degrees of correlations varied

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with the toxicogenic mechanisms of different airborne chemicals. Based on the overall $PM_{2.5}$ samples from various sources, the proinflammatory cytokine IL-6 showed significantly strong positive correlations with SO_4^{2-} and some heavy metals (Pb, As, Cu), while TNF-α and oxidative stress (ROS) had similar significant positive correlations with aerosol components of carbon fractions (OC, EC), WSIs (Ca^{2+}, Mg^{2+}), and heavy metals (Ni, Cr). The TNF-α also showed positively correlation with water soluble Cl^- and K^+, and ROS correlated with F^- and Na^+.

4 Discussion

4.1 New chemical markers for source apportionments of ambient air $PM_{2.5}$

Combustion emissions are key anthropogenic sources contributing to urban air $PM_{2.5}$, through both primary and secondary aerosols, which were 66% and 34% calculated by PMF model, respectively (Figure 1). The high concentrations of chemical markers are usually used in source analysis, such as ammonium sulfate and nitrate for secondary aerosols which are originated mainly from the gaseous precursors (e.g., NH_3, SO_2 and NO_X) (Mahilang et al., 2021), the EC, Cu, Mn, and Ni for vehicle exhaust (Srivastava et al., 2021) , the As, Pb, OC, EC, SO_4^{2-} and relatively low NO_3^-/SO_4^{2-} ratios for coal combustion(Dai et al., 2020), soluble K^+ and Cl^- for biomass burning (Jain et al., 2020). The detailed chemical species of these specific source emission $PM_{2.5}$ samples also supported the results. Moreover, low OC/EC ratio of high TC content, high NO_3^-, F^-, Na^+, Ca^{2+} and Mg^{2+}, V and Mn of automobile exhaust, Pb and As, SO_4^{2-} and NH_4^+ of coal combustion, soluble K^+ and Cl^-, and high OC/EC ratio of high TC for biomass burning found in current study (Figure 2-5), could also be corresponding potential aerosol source markers. The principal aim of this paper was to assess and contrast the chemical composition and potential harmfulness of particulate matter arising from diverse anthropogenic sources. As such, natural sources, like road dust, were not included in the source examination.

4.2 Common $PM_{2.5}$ components related to specific combustion sources

The OC/EC ratio of ambient aerosols greater than 2.0 is usually associated with secondary organic carbon (SOC) (Wang et al., 2022b), while the EC characteristics of primary $PM_{2.5}$ from various combustion emissions in current study also indicate their sources. The automobile exhaust source had high TC content and low OC/EC value with considerable EC content (Figure 2), varying with specific vehicle types (Figure S4). The contents of the carbon fractions from diesel vehicles were higher than gasoline exhausts, and the OC/EC ratios of diesel exhausts were much lower than gasoline vehicles, owing to both considerable contents of EC and OC from diesel vehicle emission $PM_{2.5}$. Some diesel vehicles showed higher EC emissions with age, so exhaust cleaning devices for them are suggested. In addition, the amounts of OC and EC in exhausts gradually decreased with the strengthened emission standards (Wong et al., 2020). In $PM_{2.5}$ samples obtained from coal combustion (Figure S5), the TC contents of bituminous coals were significantly higher than that of honeycomb coals, anthracite coals, and industrial coals, because bituminous coals contain higher volatile fraction, which is composed of organic matter. Therefore, besides the way of

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combustion and the use of combustion stoves, the coal quality related to different coal types and origins determine the carbonaceous fractions of the PMs emitted from coal combustion (Zhang et al., 2022a). In the $PM_{2.5}$ samples from biomass combustion (Figure S6), OC contents were generally higher than EC contents, except that pine branches contained higher EC and rapeseed straw had considerable contents of EC and OC. Dominated by OC (Figure S7), the concentrations of carbonaceous fractions in ambient air samples varied seasonally (Flores et al., 2020;Xu et al., 2019). Combining the TC contents and OC/EC ratios, carbonaceous components in ambient $PM_{2.5}$ mainly originate from SOC (Wang et al., 2018) and anthropogenic combustion primary emissions for OC (Kang et al., 2018), and automobile exhaust for EC (Barraza et al., 2017). Thus, to control ambient carbon aerosol pollution, besides reducing the SOC precursor emissions, controlling primary aerosols especially EC from diesel vehicles were key measures.

Airborne heavy metals are usually recognized as contributing the oxidation stress of $PM_{2.5}$. Different types of automobiles emitted diverse metal contents (Figure S8). Because Mn is a common antidetonator that delays and prevents the oxidation of hydrocarbons and increases the octane number, which not only increases the thermal efficiency of the engine but also improves the emission performance of the vehicle (Cheung et al., 2010), the Mn content was greater in gasoline vehicle exhausts than in diesel vehicles. Although there are multi-sources of traffic Pb emissions such as fuel combustion and brake wear (Wang et al., 2019;Panko et al., 2019), the automobile exhaust Pb content of gasoline vehicles were greater than diesel vehicles owing to oil combustion. Moreover, for the same vehicle type (LDDVs-1 and 2; HDDVs-1 and 2; SDGCs-1 and 2), the stricter the emission standard, the lower the exhaust metal contents. The metal contents in the $PM_{2.5}$ of trucks was higher than that of passenger cars (Wu et al., 2016). In the combustion $PM_{2.5}$ of 10 coal types (Figure S9), Pb contents were the highest than other heavy metals, similar to available findings (Zhang et al., 2020). The $PM_{2.5}$ metals from bituminous coal were significantly lower than other coal types, because indicated by the coal quality analysis, bituminous coal has a low ash content which is mainly derived from non-combustible minerals in coal. These findings suggested that coal maturity might be an important factor influencing the metal composition of particulates emitted from coal combustion (Shen et al., 2021;Zhang et al., 2021). Heavy metal contents in burned $PM_{2.5}$ varied much widely with biomass types (Figure S10), although dominated by Cr and Ni. Because of the high enrichment coefficients of some metals for crop straws (Zhang et al., 2016;Sun et al., 2019), they also released more Cr, Ni, and Co during burning than fuelwoods. Total metal emissions were highest in corn cob but lowest in peanut straw burning. The heavy metals enriched in urban ambient air $PM_{2.5}$ demonstrated a seasonal pattern (Chen et al., 2018;Hsu et al., 2016) (Figure S11). Contents of V, Co, and As were relatively low and are less affected by seasonal changes. Accordingly, supported by the metal profiles of anthropogenic combustion sources and ambient aerosols, to control the environmental airborne heavy metal pollution, the Pb, Cu and As from honeycomb, anthracite and industrial coal combustion, Cu from vehicle exhausts and especially V from light duty diesel van with the CN.III emission standard and Mn from gasoline vehicles, Cr and Ni from biomass especially crop straws burning, should be key targets.

Epidemiological studies have also shown the mortality closely related to the WSIs such as sulfate and nitrate in aerosols (Ostro et al., 2009;Liang et al., 2022). Among the WSIs contents of various automobile exhausts (Figure S12), NO_3^- and Ca^{2+}

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were the most abundant anion and cation, respectively. The high NO_3^- in the automobile $PM_{2.5}$ may be due to NO_x production during high-temperature combustion (Zhang et al., 2022b), while the high Ca^{2+} content should be related to additives in automobile fuels and calcium-based lubricants (Hao et al., 2019;Yang et al., 2019). Moreover, the exhaust WSIs decreased with the strengthened automobile emission standards. Coal combustion $PM_{2.5}$ contained relatively higher SO_4^{2-} and NH_4^+ concentrations followed by Cl^- than other WSIs species (Figure S13). Among various coal types, industrial coals emitted highest SO_4^{2-} followed by honeycomb and industrial coal with also high NH_4^+, but bituminous coals emitted low WSIs which were mainly NO_3^-, F^- and Na^+, Ca^{2+}. The WSIs emission factors of honeycomb coal were generally higher than those of lump coal (Yan et al., 2020). For biomass combustion emissions (Figure S14), Cl^- and K^+ were dominant WSIs in $PM_{2.5}$ from straw-based biomass fuels (Tao et al., 2016;Sillapapiromsuk et al., 2013), but fuelwood-based combustion emitted high NO_3^-. Plant species absolutely determine the emissions (Liao et al., 2021). Finally, there were also high levels of NO_3^-, SO_4^{2-}, and NH_4^+ in ambient air $PM_{2.5}$ (Zhang et al., 2019) (Figure S15). Consequently, implied by the WSIs species distributed in anthropogenic combustion sources and environmental $PM_{2.5}$, to control the aerosols ions pollution, the NO_3^- from vehicle exhausts and fuelwood burning, SO_4^{2-} and NH_4^+ from honeycomb, anthracite and industrial coal combustion, Cl^- and K^+ from biomass especially crop straw burning, should be principal targets, by stricter automobile emission standards or using clean coals.

4.3 $PM_{2.5}$ toxicity related to specific sources by pivotal chemical components

The complexity of the sources and compositions of atmospheric $PM_{2.5}$ leads to different toxicological effects (Newman et al., 2020;Kelly, 2021). Our results demonstrated that the toxicities of anthropogenic combustion emission $PM_{2.5}$ were much greater than the urban ambient air $PM_{2.5}$ (Figure 6), owing to the higher concentrations of specific toxic components in $PM_{2.5}$ from these sources. The supplementary information had included exhaustive cytotoxicity indicators from each individual source (Figure S16-S19). While the survival rate of cell exposed to CN.III emission standard $PM_{2.5}$ was the lowest and the capacity to induce cells to produce ROS was the highest for CN.IV, automobile exhaust had a similar potential to cause cells to produce inflammatory cytokines (Figure S16). The capability to induce IL-6 production in cells was highest in industrial coal, whereas bituminous coal had the highest survival rate of cells and TNF-α induction capacity (Figure S17). From the Figure S18 above we can see that the cytotoxicity of straw and branches was analogous, but it should be noted that the survival rate of cell of various straw varies significantly. Carbon fractions bound in $PM_{2.5}$ could be transformed into reactive metabolites and then induce ROS production in cells (Stevanovic et al., 2019). The $PM_{2.5}$ bound heavy metals could also induce ROS production through the Fenton reaction and disrupt the function of enzymes in cells (Verma et al., 2010;Sørensen et al., 2005). Water-soluble components of $PM_{2.5}$, especially water-soluble transition metal ions could accelerate the induction of free radicals, which can cause inflammatory damage (Zou et al., 2016). Oxidative stress can lead to inflammatory infiltration of neutrophils and stimulate immune cells to produce inflammatory cytokines, among which TNF-α and IL-6 play important roles in the inflammation development (Xu et al., 2020). Ultimately, excessive production of ROS leads to dysfunctional endoplasmic

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reticulum responses and dysfunctional lipid metabolism in ROS bursts can result in cell membrane damage and even cell death (Piao et al., 2018;Zhao et al., 2004).

These mechanisms were supported by the relationships between the measured components with cytotoxicity indicators of $PM_{2.5}$ from various specific sources (Figure 7). By relating to the chemical components overall, IL-6 was significantly positively correlated with SO_4^{2-}, Pb, As, and Cu, which were main contributors of coal combustion sources. Both TNF-α and ROS were significantly positively correlated with carbonaceous fractions, Ni, and Cr, which were main contributors of automobile exhausts and biomass burning; and were correlated with water soluble Ca^{2+} and Mg^{2+}, which were main contributors of automobile exhausts. Moreover, the TNF-α was also positively correlated with water soluble Cl^- and K^+, which were main contributors of biomass burning, and ROS correlated with F^- and Na^+, which were main contributors of automobile exhausts. According to the source-based aerosols cytotoxicity comparisons (Figure 6), automobile exhaust $PM_{2.5}$ induced the highest lethality and cellular ROS and TNF-α production, coal combustion $PM_{2.5}$ induced the highest cellular IL-6 production, biomass burning $PM_{2.5}$ induce considerable cellular TNF-α and ROS production. It has been reported that $PM_{2.5}$ from coal combustion decreased cell viability, increased overall DNA methylation, and led to cellular DNA oxidative damage (Møller et al., 2014). Some studies proposed that the toxicity of PAHs in PMs from biomass burning was likely underestimated (Sarigiannis et al., 2015;Yin and Xu, 2018). The OC and EC were reported significantly associated with biological responses of PMs from vehicle emissions collected in tunnels (Niu et al., 2020).

Therefore, the accumulations of some organic matters with high carbonaceous content (OC, EC) in $PM_{2.5}$ typically from automobile exhausts and biomass burning, heavy metals (Pb, As, Cu, Ni, Cr) and water-soluble anions (SO_4^{2-}, Cl^-, F^-) and cations (Ca^{2+}, Mg^{2+}, K^+) contributed by various anthropogenic combustions, might induce ROS production in cells, cause cellular damage through oxidative stress and inflammatory responses, impair cell viability and finally harm human health. To improve the urban environmental air quality for best public health benefits by controlling aerosols pollution, considering the toxicity intensity of each chemical component and their contributions from various sources to ambient aerosols, preferential targets of specific primary $PM_{2.5}$ sources and bound pollutants to be controlled are suggested as following sequence: Reducing all anthropogenic combustions, especially decreasing the automobile exhaust with high contents of EC, Ca^{2+}, Mg^{2+}, F^-, and Na^+ from diesel exhausts by strengthening the emission standards, then controlling the coal combustion with high SO_4^{2-}, Pb, As, and Cu from by replacement with low-ash clean coals, and depressing the biomass burning with high OC, Ni, Cr, Cl^-, and K^+ from crop straw emissions.

5 Conclusions

In current study, we found that 2/3 mass of urban ambient air $PM_{2.5}$ in a typical megacity of eastern China originated from primary anthropogenic combustion sources. Because of the significant differences in the chemical compositions, the $PM_{2.5}$ from both ambient air and combustion sources showed much diverse *in vitro* toxicity to the human lung epithelial cells, either

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for the environmental aerosol samples collected from different seasons, or for the direct $PM_{2.5}$ emissions from various source types and even from the specific sub-groups of each fuel source category. According to the comparative study and correlation analysis, the carbonaceous fractions (EC, OC), water-soluble ions (SO_4^{2-}, Ca^{2+}, Mg^{2+}, Na^+, K^+, F^-, Cl^-), and heavy metals (Pb, As, Cu, Ni, Cr) might play important roles in inducing cellular ROS production, causing oxidative stress and inflammation, resulting in cell injury and apoptosis, thus damage human health. These toxic pollutants accumulated in specific sources varied by the fuel properties. Combined with chemical composition and cytotoxicity sequence, the preferential controlling targets of specific combustion sources should be automobile exhaust (diesel vehicles with emission standards inferior to CN.IV), coal combustion (high ash and high sulfur coals), and biomass burning (crop straws). Although showing the synthetic effects of mixed compositions and complex sources, besides preventing the secondary aerosols from combustions, targeted reductions of these primary sources of toxic $PM_{2.5}$ direct emissions, would produce the greatest benefits for public health with improved ambient air quality. Overall, this paper provides a precise, oriented, effective, efficient, and economical composition-source-based strategies for urban aerosols pollution control. However, as a prospect, the detailed mechanisms for toxicity of PMs with complicated components from various sources and their quantitative contributions to the health effects of ambient air $PM_{2.5}$ mixture still need in-depth study.

Supplementary materials

There are 19 figures (Figure S1-S19) and 3 tables (Table S1-S3) in the Supporting Information.

Data availability

All raw data can be provided by the corresponding authors upon request.

Author contributions

XSL conceived and supervised the study; WH, YP, MT, HL, and ZZ collected the samples; WH, YP, MT, WL, HL, ZZ, GS, and LX analyzed the chemical compositions; WH, YP, and MT performed the toxicity tests; WH, YP, MT, and XSL analyzed the data; WH and XSL wrote the manuscript draft; XSL, WH, GS, and TM reviewed and edited the manuscript.

Competing interests

The authors declare that they have no conflict of interest.

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Preprint. Discussion started: 11 April 2023

References

Al-Kindi, S. G., Brook, R. D., Biswal, S., and Rajagopalan, S.: Environmental determinants of cardiovascular disease: lessons learned from air pollution, Nat. Rev. Cardiol., 17, 656-672, https://doi.org/10.1038/s41569-020-0371-2, 2020.

Bao, F., Li, M., Zhang, Y., Chen, C., and Zhao, J.: Photochemical aging of Beijing urban PM2.5: HONO production, Environ. Sci. Technol., 52, 6309-6316, https://doi.org/10.1021/acs.est.8b00538, 2018.

Bari, M. A., and Kindzierski, W. B.: Eight-year (2007–2014) trends in ambient fine particulate matter ($PM_{2.5}$) and its chemical components in the Capital Region of Alberta, Canada, Environ. Int., 91, 122-132, https://doi.org/10.1016/j.envint.2016.02.033, 2016.

Barraza, F., Lambert, F., Jorquera, H., Villalobos, A. M., and Gallardo, L.: Temporal evolution of main ambient PM2.5 sources in Santiago, Chile, from 1998 to 2012, Atmos. Chem. Phys., 17, 10093-10107, https://doi.org/10.5194/acp-17-10093-2017, 2017.

Chen, Q., Luo, X.-S., Chen, Y., Zhao, Z., Hong, Y., Pang, Y., Huang, W., Wang, Y., and Jin, L.: Seasonally varied cytotoxicity of organic components in $PM_{2.5}$ from urban and industrial areas of a Chinese megacity, Chemosphere, 230, 424-431, https://doi.org/10.1016/j.chemosphere.2019.04.226, 2019.

Chen, Y., Luo, X.-S., Zhao, Z., Chen, Q., Wu, D., Sun, X., Wu, L., and Jin, L.: Summer–winter differences of $PM_{2.5}$ toxicity to human alveolar epithelial cells (A549) and the roles of transition metals, Ecotoxicol. Environ. Saf., 165, 505-509, https://doi.org/10.1016/j.ecoenv.2018.09.034, 2018.

Cheung, K., Ntziachristos, L., Tzamkiozis, T., Schauer, J., Samaras, Z., Moore, K., and Sioutas, C.: Emissions of particulate trace elements, metals and organic species from gasoline, diesel, and biodiesel passenger vehicles and their relation to oxidative potential, Aerosol Sci. Technol., 44, 500-513, https://doi.org/10.1080/02786821003758294, 2010.

Chi, K. H., Huang, Y.-T., Nguyen, H. M., Tran, T. T.-H., Chantara, S., and Ngo, T. H.: Characteristics and health impacts of $PM_{2.5}$-bound PCDD/Fs in three Asian countries, Environ. Int., 167, 107441, https://doi.org/10.1016/j.envint.2022.107441, 2022.

Chowdhury, S., Pozzer, A., Haines, A., Klingmuller, K., Munzel, T., Paasonen, P., Sharma, A., Venkataraman, C., and Lelieveld, J.: Global health burden of ambient $PM_{2.5}$ and the contribution of anthropogenic black carbon and organic aerosols, Environ. Int., 159, 107020, https://doi.org/10.1016/j.envint.2021.107020, 2022.

Clemens, T., Turner, S., and Dibben, C.: Maternal exposure to ambient air pollution and fetal growth in North-East Scotland: A population-based study using routine ultrasound scans, Environ. Int., 107, 216-226, https://doi.org/10.1016/j.envint.2017.07.018, 2017.

Dai, Q., Bi, X., Song, W., Li, T., Liu, B., Ding, J., Xu, J., Song, C., Yang, N., and Schulze, B. C.: Residential coal combustion as a source of primary sulfate in Xi'an, China, Atmos. Environ., 196, 66-76, https://doi.org/10.1016/j.atmosenv.2018.10.002, 2019.

Dai, Q., Liu, B., Bi, X., Wu, J., Liang, D., Zhang, Y., Feng, Y., and Hopke, P. K.: Dispersion normalized PMF provides insights into the significant changes in source contributions to $PM_{2.5}$ after the COVID-19 outbreak, Environ. Sci. Technol., 54, 9917-9927, https://doi.org/10.1021/acs.est.0c02776, 2020.

Flores, R. M., Mertoğlu, E., Özdemir, H., Akkoyunlu, B. O., Demir, G., Ünal, A., and Tayanç, M.: A high-time resolution study of $PM_{2.5}$, organic carbon, and elemental carbon at an urban traffic site in Istanbul, Atmos. Environ., 223, 117241, https://doi.org/10.1016/j.atmosenv.2019.117241, 2020.

Hao, Y., Gao, C., Deng, S., Yuan, M., Song, W., Lu, Z., and Qiu, Z.: Chemical characterisation of $PM_{2.5}$ emitted from motor vehicles powered by diesel, gasoline, natural gas and methanol fuel, Sci. Total Environ., 674, 128-139, https://doi.org/10.1016/j.scitotenv.2019.03.410, 2019.

Hsu, C.-Y., Chiang, H.-C., Lin, S.-L., Chen, M.-J., Lin, T.-Y., and Chen, Y.-C.: Elemental characterization and source apportionment of PM_{10} and $PM_{2.5}$ in the western coastal area of central Taiwan, Sci. Total Environ., 541, 1139-1150, https://doi.org/10.1016/j.scitotenv.2015.09.122, 2016.

Huang, W., Pang, Y., Luo, X.-S., Chen, Q., Wu, L., Tang, M., Hong, Y., Chen, J., and Jin, L.: The cytotoxicity and genotoxicity of $PM_{2.5}$ during a snowfall event in different functional areas of a megacity, Sci. Total Environ., 741, 140267, https://doi.org/10.1016/j.scitotenv.2020.140267, 2020.

Jain, S., Sharma, S., Vijayan, N., and Mandal, T.: Seasonal characteristics of aerosols ($PM_{2.5}$ and PM_{10}) and their source apportionment using PMF: a four year study over Delhi, India, Environ. Pollut., 262, 114337,

https://doi.org/10.5194/egusphere-2023-598
Preprint. Discussion started: 11 April 2023

https://doi.org/10.1016/j.envpol.2020.114337, 2020.

Jesus, R. M. d., Mosca, A. C., Guarieiro, A. L., Rocha, G. O. d., and Andrade, J. B. d.: In vitro evaluation of oxidative stress caused by fine particles ($PM_{2.5}$) exhausted from heavy-duty vehicles using diesel/biodiesel blends under real world conditions, J. Braz. Chem. Soc., 29, 1268-1277, https://doi.org/10.21577/0103-5053.20170223, 2018.

Jia, Y.-Y., Wang, Q., and Liu, T.: Toxicity research of $PM_{2.5}$ compositions in vitro, Int. J. Environ. Res. Public. Health, 14, 232, https://doi.org/10.3390/ijerph14030232, 2017.

Jia, Y., Li, X., Nan, A., Zhang, N., Chen, L., Zhou, H., Zhang, H., Qiu, M., Zhu, J., and Ling, Y.: Circular RNA 406961 interacts with ILF2 to regulate $PM_{2.5}$-induced inflammatory responses in human bronchial epithelial cells via activation of STAT3/JNK pathways, Environ. Int., 141, 105755, https://doi.org/10.1016/j.envint.2020.105755, 2020.

Kang, M., Ren, L., Ren, H., Zhao, Y., Kawamura, K., Zhang, H., Wei, L., Sun, Y., Wang, Z., and Fu, P.: Primary biogenic and anthropogenic sources of organic aerosols in Beijing, China: Insights from saccharides and n-alkanes, Environ. Pollut., 243, 1579-1587, https://doi.org/10.1016/j.envpol.2018.09.118, 2018.

Kelly, F.: Air pollution and chronic bronchitis: the evidence firms up, Thorax, http://dx.doi.org/10.1136/thoraxjnl-2021-216883, 2021.

Lelieveld, S., Wilson, J., Dovrou, E., Mishra, A., Lakey, P. S. J., Shiraiwa, M., Poschl, U., and Berkemeier, T.: Hydroxyl Radical Production by Air Pollutants in Epithelial Lining Fluid Governed by Interconversion and Scavenging of Reactive Oxygen Species, Environ Sci Technol, 55, 14069-14079, https://doi.org/10.1021/acs.est.1c03875, 2021.

Li, H., Zhao, Z., Luo, X.-S., Fang, G., Zhang, D., Pang, Y., Huang, W., Mehmood, T., and Tang, M.: Insight into urban PM2.5 chemical composition and environmentally persistent free radicals attributed human lung epithelial cytotoxicity, Ecotoxicol. Environ. Saf., 234, 113356, https://doi.org/10.1016/j.ecoenv.2022.113356, 2022.

Liang, R., Chen, R., Yin, P., van Donkelaar, A., Martin, R. V., Burnett, R., Cohen, A. J., Brauer, M., Liu, C., and Wang, W.: Associations of long-term exposure to fine particulate matter and its constituents with cardiovascular mortality: A prospective cohort study in China, Environ. Int., 162, 107156, https://doi.org/10.1016/j.envint.2022.107156, 2022.

Liao, X., Zhang, S., Wang, X., Shao, J., Zhang, X., Wang, X., Yang, H., and Chen, H.: Co-combustion of wheat straw and camphor wood with coal slime: Thermal behavior, kinetics, and gaseous pollutant emission characteristics, Energy, 234, 1-11, https://doi.org/10.1016/j.energy.2021.121292, 2021.

Lin, Y.-C., Li, Y.-C., Amesho, K. T., Shangdiar, S., Chou, F.-C., and Cheng, P.-C.: Chemical characterization of $PM_{2.5}$ emissions and atmospheric metallic element concentrations in $PM_{2.5}$ emitted from mobile source gasoline-fueled vehicles, Sci. Total Environ., 739, 139942, https://doi.org/10.1016/j.scitotenv.2020.139942, 2020.

Mahilang, M., Deb, M. K., and Pervez, S.: Biogenic secondary organic aerosols: A review on formation mechanism, analytical challenges and environmental impacts, Chemosphere, 262, 127771, https://doi.org/10.1016/j.chemosphere.2020.127771, 2021.

McDuffie, E. E., Martin, R. V., Spadaro, J. V., Burnett, R., Smith, S. J., O'Rourke, P., Hammer, M. S., van Donkelaar, A., Bindle, L., Shah, V., Jaegle, L., Luo, G., Yu, F., Adeniran, J. A., Lin, J., and Brauer, M.: Source sector and fuel contributions to ambient $PM_{2.5}$ and attributable mortality across multiple spatial scales, Nat. Commun., 12, 3594, https://doi.org/10.1038/s41467-021-23853-y, 2021.

Møller, P., Danielsen, P. H., Karottki, D. G., Jantzen, K., Roursgaard, M., Klingberg, H., Jensen, D. M., Christophersen, D. V., Hemmingsen, J. G., Cao, Y., and Loft, S.: Oxidative stress and inflammation generated DNA damage by exposure to air pollution particles, Mutat. Res.-Rev. Mutat. Res., 762, 133-166, https://doi.org/10.1016/j.mrrev.2014.09.001, 2014.

Newman, J. D., Bhatt, D. L., Rajagopalan, S., Balmes, J. R., Brauer, M., Breysse, P. N., Brown, A. G. M., Carnethon, M. R., Cascio, W. E., Collman, G. W., Fine, L. J., Hansel, N. N., Hernandez, A., Hochman, J. S., Jerrett, M., Joubert, B. R., Kaufman, J. D., Malik, A. O., Mensah, G. A., Newby, D. E., Peel, J. L., Siegel, J., Siscovick, D., Thompson, B. L., Zhang, J., and Brook, R. D.: Cardiopulmonary Impact of Particulate Air Pollution in High-Risk Populations: JACC State-of-the-Art Review, J. Am. Coll. Cardiol., 76, 2878-2894, https://doi.org/10.1016/j.jacc.2020.10.020, 2020.

Niu, X., Chuang, H.-C., Wang, X., Ho, S. S. H., Li, L., Qu, L., Chow, J. C., Watson, J. G., Sun, J., Lee, S., Cao, J., and Ho, K. F.: Cytotoxicity of $PM_{2.5}$ vehicular emissions in the Shing Mun Tunnel, Hong Kong, Environ. Pollut., 263, 114386, https://doi.org/10.1016/j.envpol.2020.114386, 2020.

Ostro, B., Roth, L., Malig, B., and Marty, M.: The effects of fine particle components on respiratory hospital admissions in children, Environ. Health Perspect., 117, 475-480, https://doi.org/10.1289/ehp.11848, 2009.

Pang, Y., Huang, W., Luo, X.-S., Chen, Q., Zhao, Z., Tang, M., Hong, Y., Chen, J., and Li, H.: In-vitro human lung cell injuries

https://doi.org/10.5194/egusphere-2023-598
Preprint. Discussion started: 11 April 2023

induced by urban $PM_{2.5}$ during a severe air pollution episode: variations associated with particle components, Ecotoxicol. Environ. Saf., 206, 111406, https://doi.org/10.1016/j.ecoenv.2020.111406, 2020.

Panko, J. M., Hitchcock, K. M., Fuller, G. W., and Green, D.: Evaluation of Tire Wear Contribution to $PM_{2.5}$ in Urban Environments, Atmosphere, 10, 99, https://doi.org/10.3390/atmos10020099, 2019.

Piao, M. J., Ahn, M. J., Kang, K. A., Ryu, Y. S., Hyun, Y. J., Shilnikova, K., Zhen, A. X., Jeong, J. W., Choi, Y. H., Kang, H. K., Koh, Y. S., and Hyun, J. W.: Particulate matter 2.5 damages skin cells by inducing oxidative stress, subcellular organelle dysfunction, and apoptosis, Arch. Toxicol., 92, 2077-2091, https://doi.org/10.1007/s00204-018-2197-9, 2018.

Sahu, S. K., Mangaraj, P., Beig, G., Samal, A., Pradhan, C., Dash, S., and Tyagi, B.: Quantifying the high resolution seasonal emission of air pollutants from crop residue burning in India, Environ. Pollut., 286, 117165, https://doi.org/10.1016/j.envpol.2021.117165, 2021.

Sarigiannis, D. A., Karakitsios, S. P., Zikopoulos, D., Nikolaki, S., and Kermenidou, M.: Lung cancer risk from PAHs emitted from biomass combustion, Environ. Res., 137, 147-156, https://doi.org/10.1016/j.envres.2014.12.009, 2015.

Shen, H., Luo, Z., Xiong, R., Liu, X., Zhang, L., Li, Y., Du, W., Chen, Y., Cheng, H., Shen, G., and Tao, S.: A critical review of pollutant emission factors from fuel combustion in home stoves, Environ. Int., 157, 106841, https://doi.org/10.1016/j.envint.2021.106841, 2021.

Sillapapiromsuk, S., Chantara, S., Tengjaroenkul, U., Prasitwattanaseree, S., and Prapamontol, T.: Determination of PM_{10} and its ion composition emitted from biomass burning in the chamber for estimation of open burning emissions, Chemosphere, 93, 1912-1919, https://doi.org/10.1016/j.chemosphere.2013.06.071, 2013.

Smith, S. J.: Cleaning cars, grid and air, Nat. Energy, 6, 19-20, https://doi.org/10.1038/s41560-020-00769-3, 2021.

Sørensen, M., Schins, R. P. F., Hertel, O., and Loft, S.: Transition Metals in Personal Samples of $PM_{2.5}$ and Oxidative Stress in Human Volunteers, Cancer Epidemiol. Biomarkers Prev., 14, 1340-1343, https://doi.org/10.1158/1055-9965.Epi-04-0899, 2005.

Srivastava, D., Xu, J., Vu, T. V., Liu, D., Li, L., Fu, P., Hou, S., Moreno Palmerola, N., Shi, Z., and Harrison, R. M.: Insight into $PM_{2.5}$ sources by applying positive matrix factorization (PMF) at urban and rural sites of Beijing, Atmos. Chem. Phys., 21, 14703-14724, https://doi.org/10.5194/acp-21-14703-2021, 2021.

Stevanovic, S., Gali, N. K., Salimi, F., Brown, R., Ning, Z., Cravigan, L., Brimblecombe, P., Bottle, S., and Ristovski, Z. D.: Diurnal profiles of particle-bound ROS of $PM_{2.5}$ in urban environment of Hong Kong and their association with $PM_{2.5}$, black carbon, ozone and PAHs, Atmos. Environ., 219, 117023, https://doi.org/10.1016/j.atmosenv.2019.117023, 2019.

Sun, J., Shen, Z., Zhang, Y., Zhang, Q., Lei, Y., Huang, Y., Niu, X., Xu, H., Cao, J., Ho, S. S. H., and Li, X.: Characterization of $PM_{2.5}$ source profiles from typical biomass burning of maize straw, wheat straw, wood branch, and their processed products (briquette and charcoal) in China, Atmos. Environ., 205, 36-45, https://doi.org/10.1016/j.atmosenv.2019.02.038, 2019.

Sun, J., Shen, Z., Niu, X., Zhang, Y., Zhang, B., Zhang, T., He, K., Xu, H., Liu, S., Ho, S. S. H., Li, X., and Cao, J.: Cytotoxicity and Potential Pathway to Vascular Smooth Muscle Cells Induced by $PM_{2.5}$ Emitted from Raw Coal Chunks and Clean Coal Combustion, Environ Sci Technol, 54, 14482-14493, https://doi.org/10.1021/acs.est.0c02236, 2020.

Tao, J., Zhang, L., Zhang, R., Wu, Y., Zhang, Z., Zhang, X., Tang, Y., Cao, J., and Zhang, Y.: Uncertainty assessment of source attribution of $PM_{2.5}$ and its water-soluble organic carbon content using different biomass burning tracers in positive matrix factorization analysis — a case study in Beijing, China, Sci. Total Environ., 543, 326-335, https://doi.org/10.1016/j.scitotenv.2015.11.057, 2016.

Tuet, W. Y., Liu, F., de Oliveira Alves, N., Fok, S., Artaxo, P., Vasconcellos, P., Champion, J. A., and Ng, N. L.: Chemical oxidative potential and cellular oxidative stress from open biomass burning aerosol, Environ. Sci. Technol. Lett., 6, 126-132, https://doi.org/10.1021/acs.estlett.9b00060, 2019.

Verma, V., Shafer, M. M., Schauer, J. J., and Sioutas, C.: Contribution of transition metals in the reactive oxygen species activity of PM emissions from retrofitted heavy-duty vehicles, Atmos. Environ., 44, 5165-5173, https://doi.org/10.1016/j.atmosenv.2010.08.052, 2010.

Wang, L., Niu, D., Fan, H., and Long, X.: Urban configuration and $PM_{2.5}$ concentrations: Evidence from 330 Chinese cities, Environ. Int., 161, 107129, https://doi.org/10.1016/j.envint.2022.107129, 2022a.

Wang, M., Duan, Y., Xu, W., Wang, Q., Zhang, Z., Yuan, Q., Li, X., Han, S., Tong, H., and Huo, J.: Measurement report: Characterisation and sources of the secondary organic carbon in a Chinese megacity over 5 years from 2016 to 2020, Atmos. Chem. Phys., 22, 12789-12802, https://doi.org/10.5194/acp-22-12789-2022, 2022b.

https://doi.org/10.5194/egusphere-2023-598
Preprint. Discussion started: 11 April 2023

Wang, S., Hu, G., Yan, Y., Wang, S., Yu, R., and Cui, J.: Source apportionment of metal elements in $PM_{2.5}$ in a coastal city in Southeast China: Combined Pb-Sr-Nd isotopes with PMF method, Atmos. Environ., 198, 302-312, https://doi.org/10.1016/j.atmosenv.2018.10.056, 2019.

Wang, T., Tian, M., Ding, N., Yan, X., Chen, S.-J., Mo, Y.-Z., Yang, W.-Q., Bi, X.-H., Wang, X.-M., and Mai, B.-X.: Semivolatile Organic Compounds (SOCs) in Fine Particulate Matter ($PM_{2.5}$) during Clear, Fog, and Haze Episodes in Winter in Beijing, China, Environ. Sci. Technol., 52, 5199-5207, https://doi.org/10.1021/acs.est.7b06650, 2018.

Wang, Y., Wang, M., Li, S., Sun, H., Mu, Z., Zhang, L., Li, Y., and Chen, Q.: Study on the oxidation potential of the water-soluble components of ambient $PM_{2.5}$ over Xi'an, China: Pollution levels, source apportionment and transport pathways, Environ. Int., 136, 105515, https://doi.org/10.1016/j.envint.2020.105515, 2020.

Weagle, C. L., Snider, G., Li, C., van Donkelaar, A., Philip, S., Bissonnette, P., Burke, J., Jackson, J., Latimer, R., and Stone, E.: Global sources of fine particulate matter: interpretation of $PM_{2.5}$ chemical composition observed by SPARTAN using a global chemical transport model, Environ. Sci. Technol., 52, 11670-11681, https://doi.org/10.1021/acs.est.8b01658, 2018.

Wong, Y. K., Huang, X., Louie, P. K., Yu, A. L., Chan, D. H., and Yu, J. Z.: Tracking separate contributions of diesel and gasoline vehicles to roadside $PM_{2.5}$ through online monitoring of volatile organic compounds and $PM_{2.5}$ organic and elemental carbon: a 6-year study in Hong Kong, Atmos. Chem. Phys., 20, 9871-9882, https://doi.org/10.5194/acp-20-9871-2020, 2020.

Wu, B., Shen, X., Cao, X., Yao, Z., and Wu, Y.: Characterization of the chemical composition of $PM_{2.5}$ emitted from on-road China III and China IV diesel trucks in Beijing, China, Sci. Total Environ., 551, 579-589, https://doi.org/10.1016/j.scitotenv.2016.02.048, 2016.

Wu, D., Zheng, H., Li, Q., Jin, L., Lyu, R., Ding, X., Huo, Y., Zhao, B., Jiang, J., and Chen, J.: Toxic potency-adjusted control of air pollution for solid fuel combustion, Nat. Energy, 7, 194-202, https://doi.org/10.1038/s41560-021-00951-1, 2022.

Xu, F., Shi, X., Qiu, X., Jiang, X., Fang, Y., Wang, J., Hu, D., and Zhu, T.: Investigation of the chemical components of ambient fine particulate matter ($PM_{2.5}$) associated with in vitro cellular responses to oxidative stress and inflammation, Environ. Int., 136, 105475, https://doi.org/10.1016/j.envint.2020.105475, 2020.

Xu, W., Liu, X., Liu, L., Dore, A. J., Tang, A., Lu, L., Wu, Q., Zhang, Y., Hao, T., Pan, Y., Chen, J., and Zhang, F.: Impact of emission controls on air quality in Beijing during APEC 2014: Implications from water-soluble ions and carbonaceous aerosol in PM2.5 and their precursors, Atmos. Environ., 210, 241-252, https://doi.org/10.1016/j.atmosenv.2019.04.050, 2019.

Yan, Q., Kong, S., Yan, Y., Liu, H., Wang, W., Chen, K., Yin, Y., Zheng, H., Wu, J., Yao, L., Zeng, X., Cheng, Y., Zheng, S., Wu, F., Niu, Z., Zhang, Y., Zheng, M., Zhao, D., Liu, D., and Qi, S.: Emission and simulation of primary fine and submicron particles and water-soluble ions from domestic coal combustion in China, Atmos. Environ., 224, https://doi.org/10.1016/j.atmosenv.2020.117308, 2020.

Yang, H.-H., Dhital, N. B., Wang, L.-C., Hsieh, Y.-S., Lee, K.-T., Hsu, Y.-T., and Huang, S.-C.: Chemical Characterization of Fine Particulate Matter in Gasoline and Diesel Vehicle Exhaust, Aerosol and Air Quality Research, 19, 1439-1449, https://doi.org/10.4209/aaqr.2019.04.0191, 2019.

Yin, H., and Xu, L.: Comparative study of PM10/PM2.5-bound PAHs in downtown Beijing, China: Concentrations, sources, and health risks, J. Clean Prod., 177, 674-683, https://doi.org/10.1016/j.jclepro.2017.12.263, 2018.

Zhang, J., Liu, L., Xu, L., Lin, Q., Zhao, H., Wang, Z., Guo, S., Hu, M., Liu, D., Shi, Z., Huang, D., and Li, W.: Exploring wintertime regional haze in northeast China: role of coal and biomass burning, Atmos. Chem. Phys., 20, 5355-5372, https://doi/org/10.5194/acp-20-5355-2020, 2020.

Zhang, L., Liu, Y., and Hao, L.: Contributions of open crop straw burning emissions to $PM_{2.5}$ concentrations in China, Environmental Research Letters, 11, https://doi.org/10.1088/1748-9326/11/1/014014, 2016.

Zhang, Q., Li, Z., Shen, Z., Zhang, T., Zhang, Y., Sun, J., Zeng, Y., Xu, H., Wang, Q., Hang Ho, S. S., and Cao, J.: Source profiles of molecular structure and light absorption of $PM_{2.5}$ brown carbon from residential coal combustion emission in Northwestern China, Environ. Pollut., 299, 118866, https://doi.org/10.1016/j.envpol.2022.118866, 2022a.

Zhang, W., Bi, X., Zhang, Y., Wu, J., and Feng, Y.: Diesel vehicle emission accounts for the dominate NOx source to atmospheric particulate nitrate in a coastal city: Insights from nitrate dual isotopes of $PM_{2.5}$, Atmospheric Research, 278, 106328, https://doi.org/10.1016/j.atmosres.2022.106328, 2022b.

Zhang, X., Zhao, X., Ji, G., Ying, R., Shan, Y., and Lin, Y.: Seasonal variations and source apportionment of water-soluble

https://doi.org/10.5194/egusphere-2023-598
Preprint. Discussion started: 11 April 2023

inorganic ions in $PM_{2.5}$ in Nanjing, a megacity in southeastern China, J. Atmos. Chem., 76, 73-88, https://doi.org/10.1007/s10874-019-09388-z, 2019.

Zhang, Y., Shen, Z., Sun, J., Zhang, L., Zhang, B., Zou, H., Zhang, T., Hang Ho, S. S., Chang, X., Xu, H., Wang, T., and Cao, J.: Parent, alkylated, oxygenated and nitrated polycyclic aromatic hydrocarbons in $PM_{2.5}$ emitted from residential biomass burning and coal combustion: A novel database of 14 heating scenarios, Environ. Pollut., 268, 115881, https://doi.org/10.1016/j.envpol.2020.115881, 2021.

Zhao, K., Zhao, G. M., Wu, D., Soong, Y., Birk, A. V., Schiller, P. W., and Szeto, H. H.: Cell-permeable peptide antioxidants targeted to inner mitochondrial membrane inhibit mitochondrial swelling, oxidative cell death, and reperfusion injury, J Biol Chem, 279, 34682-34690, https://doi.org/10.1074/jbc.M402999200, 2004.

Zhao, X., Zhou, W., Han, L., and Locke, D.: Spatiotemporal variation in $PM_{2.5}$ concentrations and their relationship with socioeconomic factors in China's major cities, Environ. Int., 133, 105145, https://doi.org/10.1016/j.envint.2019.105145, 2019.

Zou, Y., Jin, C., Su, Y., Li, J., and Zhu, B.: Water soluble and insoluble components of urban $PM_{2.5}$ and their cytotoxic effects on epithelial cells (A549) in vitro, Environ. Pollut., 212, 627-635, https://doi.org/10.1016/j.envpol.2016.03.022, 2016.

https://doi.org/10.5194/egusphere-2023-598
Preprint. Discussion started: 11 April 2023

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Captions of figures

Figure 1. PMF factor profiles and source percentages of secondary aerosol, automobile exhaust, coal combustion, and biomass burning contributing to urban ambient air $PM_{2.5}$.

Figure 2. Carbon contents (mg kg^{-1}) and ratio in $PM_{2.5}$ from various specific sources (n=10 for each combustion source and
595 n=16 for urban ambient air).

Figure 3. Heavy metal contents (mg kg^{-1}) in $PM_{2.5}$ from various specific sources (n=10 for each combustion source and n=16 for urban ambient air).

Figure 4. Water-soluble ion (WSI) contents (mg kg^{-1}) in $PM_{2.5}$ from various specific sources (n=10 for each combustion source and n=16 for urban ambient air).

600 **Figure 5.** Cumulated typical measured components (mg kg^{-1}) in $PM_{2.5}$ from various specific sources (n=10 for each combustion source and n=16 for urban ambient air).

Figure 6. Cell viability, oxidative stress and inflammation levels of human alveolar epithelial cell lines (A549) exposed to $PM_{2.5}$ suspension (80 mg L^{-1}) from various specific sources (n=10 for each combustion source and n=16 for urban ambient air).

605 **Figure 7.** Overall correlations between typical cellular toxicological responses and chemical compositions of $PM_{2.5}$ from various specific sources (*$p < 0.05$，#$p<0.01$; n=46).

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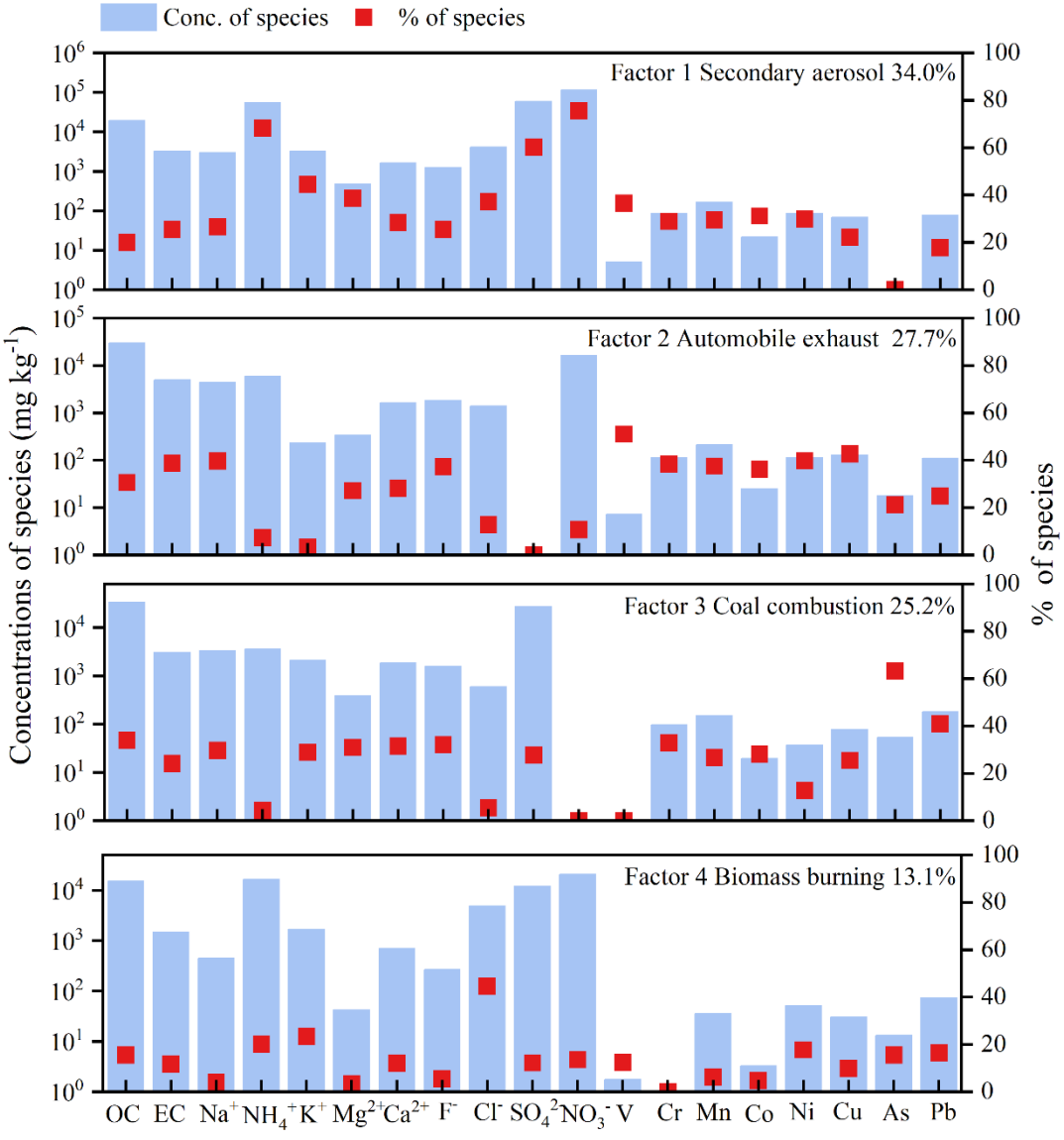

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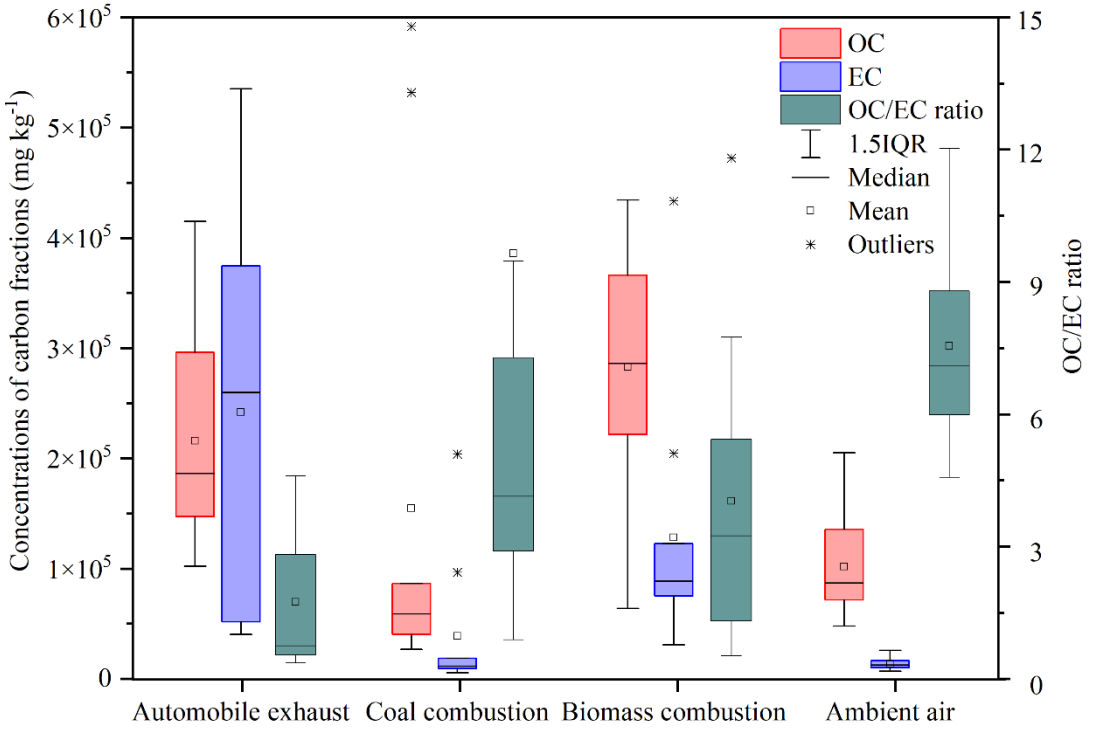

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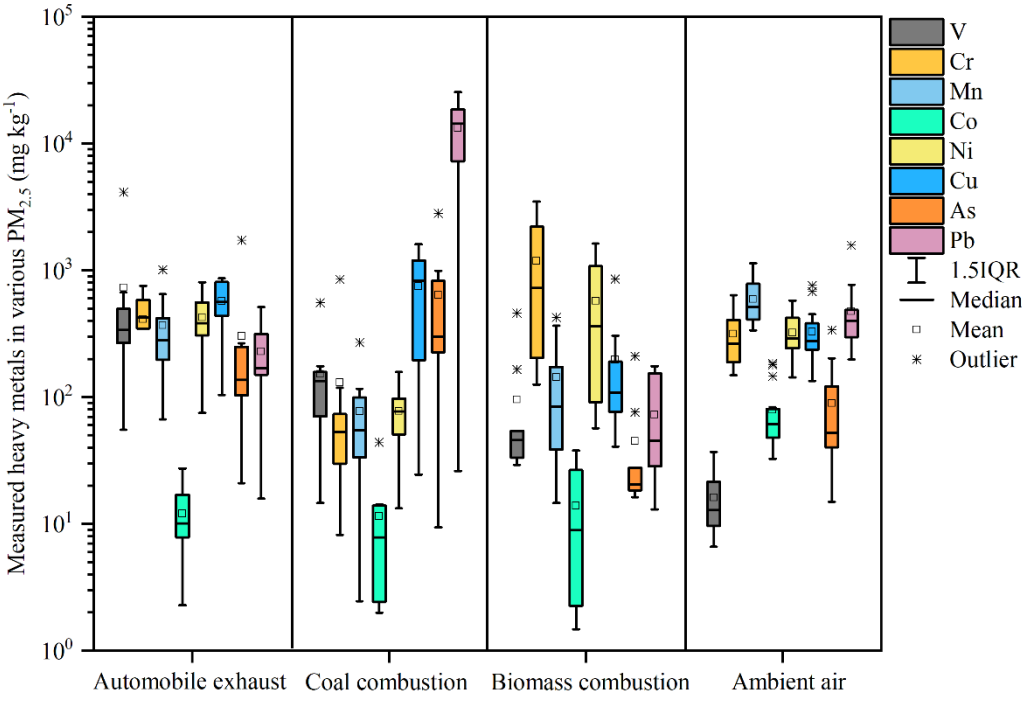

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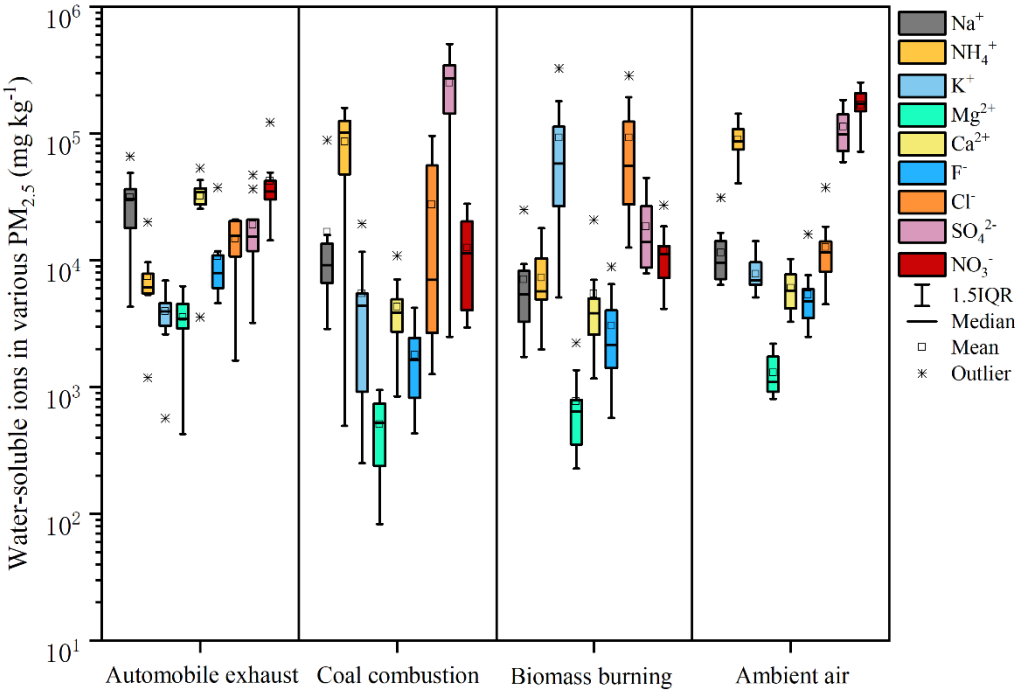

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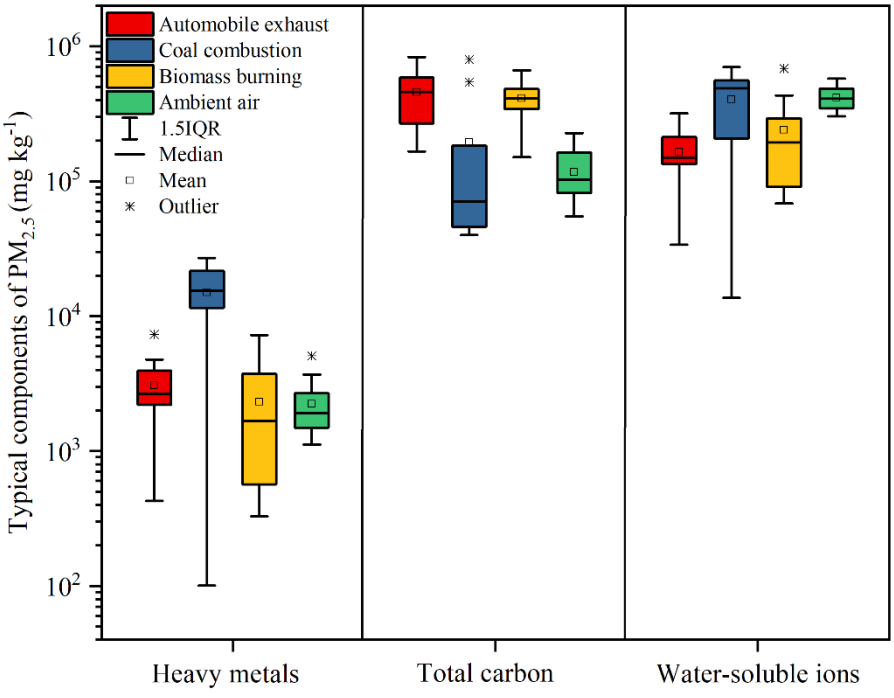

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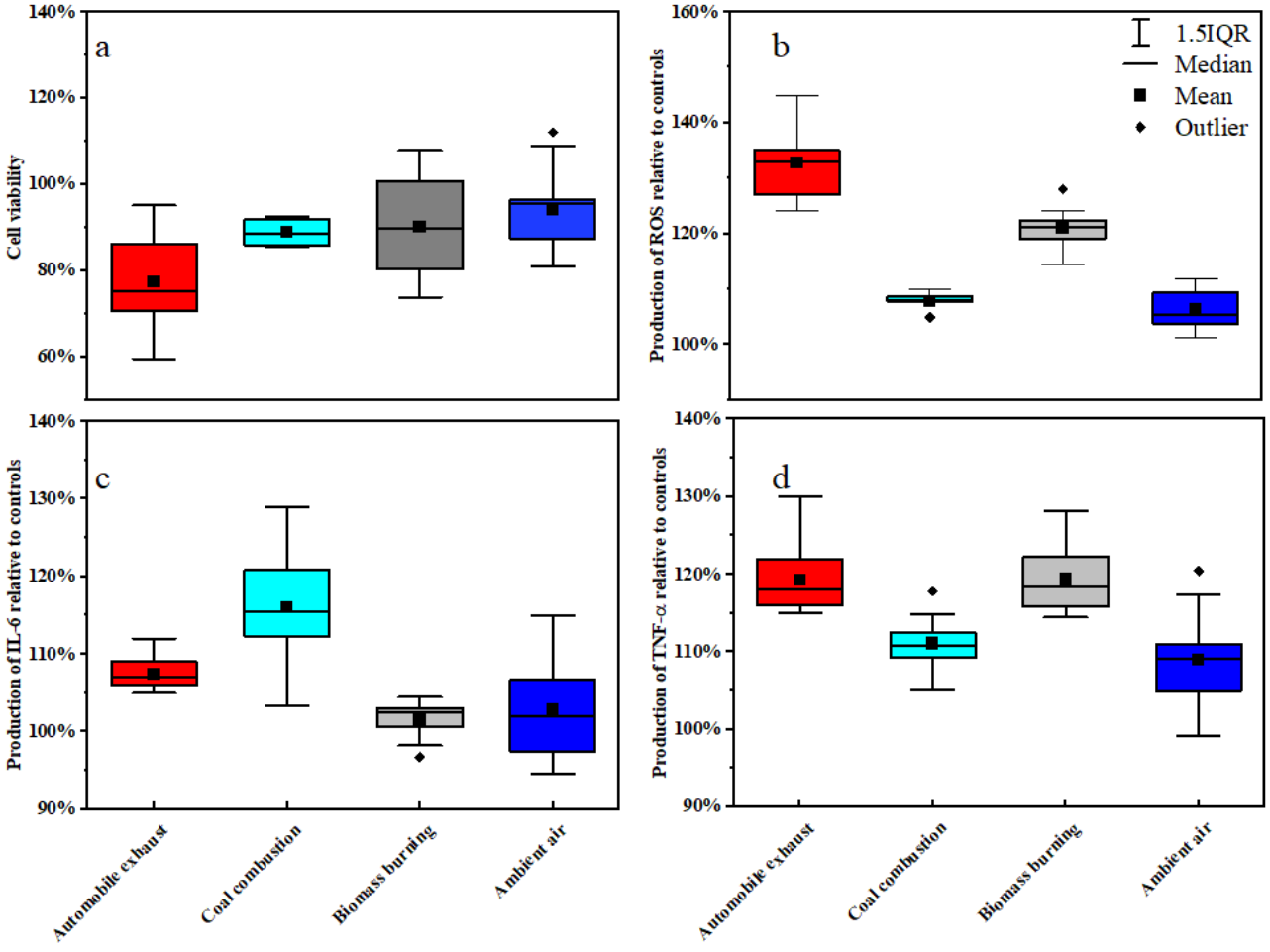

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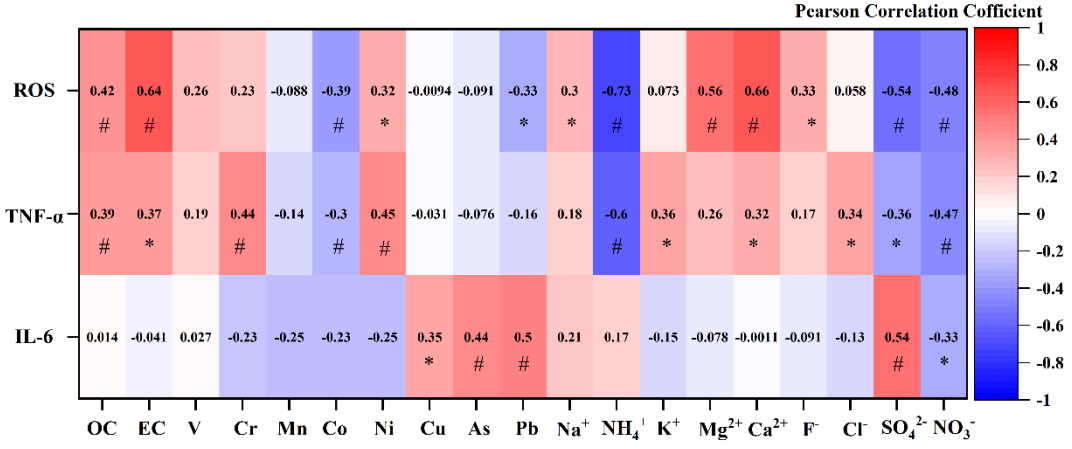

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