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Comparative Analysis of Real-Emitted Particulate Matter and PM-Bound Chemicals from Residential and Automotive Sources: A Case Study in Poland

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Abstract: The awareness of environmental pollution has been continuously growing in recent decades and is currently reaching its maximum. Europe and most developed countries are determined to ensure safe breathing air for their citizens, and the measures to do so are stricter than ever before. Combustion procedures remain the primary means of producing energy and warmth in Poland. Among the notable constituents of flue gases produced as a result of fuel combustion, solid particles (or particulate matter) hold significant prominence. The paper presents the chemical characterisation of particulate matter emitted from stationary and automotive emission sources. Stationary emission sources included the combustion process of fossil fuels (soft wood, bituminous coal, ecopea coal, culm) in domestic heating units and the process of combustion of bituminous coal in a power plant. Automotive emission sources included light duty and medium duty vehicles fuelled by diesel. Exhaust toxicity tests were carried out maintaining the real conditions of PM emission. In all field measurements particulate matter was gravimetrically measured and collected on quartz or glass fibre filters. Subsequently, the content of carbonaceous fraction, inorganic ions, and metals and metalloids was analyzed using different analytical techniques. The chemical composition of the particulate matter differed depending on the emission source. With respect to stationary combustion sources, the main factors determining solid particle emission are related primarily to the fuel quality. The duty of vehicles was also a factor that influenced the chemical characterisation of the particulate matter emitted from the engines.

Keywords: particulate matter; stationary emission sources; mobile emission sources; combustion processes; solid fuels; liquid fuels

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1. Introduction

Atmosphere protection is one of the most important actions undertaken by governments in the entire world. Air pollution is the largest risk that affects both environment and human health. Particulate matter and PM-bound chemicals inhaled into the lungs destroy the natural antioxidative barrier in an organism, causing serious damage to cells, which, in turn, result in cardiovascular and inflammatory diseases and, sometimes, even in premature deaths [1]. Despite many programmes toward cleaner atmosphere set up by the European Union, levels of particulate matter concentration above EU standards are seen across the Old Continent. According to data presented by the European Environmental Agency, Poland (together with Italy) is still the country most polluted by particulate matter [2]. This proves that multidisciplinary actions toward decreasing human exposure to pollutants and toward limitation their negative impact on ecosystems are still reasonable.

In South Poland, residential heating and traffic-related emission together with industrial emission, soil emission, and secondary inorganic aerosols have been reported as the main sources of atmospheric pollution [3–7]. According to the new nomenclature proposed by the Environmental Protection Agency of the United States, residential heating is an example of a non-point emission source, industrial emission is a point emission source, and automotive emission belongs to on-road sources. All of them may be classified as low-stack emission, what refers to the emission of harmful gases and particulate matter at a level lower than 40 m above the ground [8,9]. The low-stack related pollutants directly affect human bodies and health. Therefore, it is essential to keep these sources continuously examined and controlled.

Particulate matter is an active carrier of many chemical compounds, both organic and inorganic. An active character of PM is related to the number of processes that are ongoing in the flue gas duct or in exhaust system of engine cars. Reactions of nucleation, condensation, and agglomeration occur which cause continuous changes in the chemical composition of PM and in size of aerodynamic diameter (AD) of particles [10]. PM_{10} and $PM_{2.5}$ are classifications of particulate matter by AD factor, commonly used to measure air quality and potential health risks. PM_{10} refers to particulate matter with a diameter of 10 μm or smaller. These particles are small enough to be inhaled into the upper respiratory system. $PM_{2.5}$, on the other hand, refers to particulate matter with a diameter of 2.5 μm or smaller. These particles are even finer and can penetrate deeper into the respiratory system and lungs and even enter the bloodstream, posing a greater health risk [11].

The emission ratios of particulate matter differ depending on fuel and stove or engine applied, as well as on the operation conditions of the combustion process [12]. The implementation of exhaust aftertreatment systems, such as three-way catalysts or diesel oxidation catalysts in automotive solutions [13] and desulphurization plants and electrostatic precipitators [14,15] in industrial utilities (i.e., thermal power plants) improves the quality of exhausts released to the atmosphere. Similarly, many works around the world are conducted on exhaust aftertreatment systems for the purposes of residential heating, i.e., honeycomb Pt-based catalysts [16,17].

Regarding residential heating, coal and wood are usually used for heat and electricity generation. Despite many programmes for the installation of cogeneration systems and eco-design recommendations for the architecture of domestic heating units, due to current geopolitical situation worldwide, fossil fuels of doubtful quality are frequently used. The usage of such fuels in stoves not adapted to the requirements of eco-design directive creates the process of combustion inefficient. This results in high emission factors of particulate matter and other PM-bound components [12,18].

In Poland, there exist 19 power plants and 23 thermal power facilities fuelled by both bituminous and lignite coal as well as biomass. According to data from 2022 [19], the collective usage of coal for generating heat and electricity exceeded 70% in 2021. Furthermore, the prospects of transitioning away from coal as the predominant primary energy source are considerably extensive [20]. The combustion of fossil fuels in industrial processes also gives rise to particulate matter emissions. The quantities of pollutants emanating from power and thermal plants are under constant surveillance. Industrial establishments are mandated to cleanse flue gases before releasing them into the atmosphere, achieved through the installation of post-treatment systems like denitrification, dust extraction, or desulfurization units. Emissions originating from coal-fired power and thermal facilities raise substantial concerns due to their capacity for long-distance transport, adverse impact on human health, visibility in the atmosphere, and harm to vegetation [21–24].

Automotive emissions are one of the leading sources of air pollution with a significant share in total particulate emissions during heating and non-heating seasons, particularly in urban areas [25]. According to the latest data presented by the European Automobile Manufacturers Association (ACEA) in 2020 there were more than 246 million vehicles in use in the European Union [26]. In 2021 approximately 60% of newly registered passenger vehicles were diesel (20%) and gasoline-fuelled (40%) cars. In turn, new trucks and vans are mostly fuelled by diesel, sharing more than 96% and 90%, respectively, of the total registered medium- and heavy-duty vehicles. As the share of light-duty vehicles (LDVs) equipped with gasoline engines is higher than that of LDVs with diesel engines, it is obvious that current research trends in automotive branch are directed toward gasoline-fuelled and hybrid cars. Furthermore, the Volkswagen emissions scandal, popularly known as the 'diesel gate', caused, as the main aftermath, a decreasing popularity of light-duty diesel vehicles among European drivers. However, it is true that "diesel gate" run the machinery of improvements in automotive legislation and diesel particulate filters (DPFs) to eliminate PM emission and selective catalytic reduction to eliminate NO_x emission was finally implemented [27]. Difficulties with afterburning and regeneration process of DPFs have caused these catalytic reactors to be illegally removed from exhaust systems even in 2–3 years old cars.

Diesel engines are characterised by significantly higher torque than gasoline engines as they have larger cylinders and longer strokes. Furthermore, diesel engines are able to extract more energy from fuel as they operate at higher compression ratio [28]. Therefore, they are successfully used in vehicles of medium and heavy duty. Furthermore, it is not predicted that the number of medium-duty vehicles (MDV) and heavy-duty vehicles (HDV) will decrease. For these reasons, it seems to be adjustable to continue the examinations on emission of pollutants, especially of particulate matter, from diesel-fuelled vehicles as well.

Here we present the chemical characterisation of particulate matter generated in combustion processes of different types of fuel in both stationary and automotive sources. Field measurements at all emission sources were carried out under real conditions 'as it is'. Hence, the results provide valuable information on real exposure to PM and PM-bound chemicals and allow us to understand the nature of emitted pollutants. The final goal of this work was to identify characteristic components per each emission source, for the purposes of further work concerning the optimisation of macro tracer serving as a PM source apportionment technique.

2. Materials and Methods

2.1. Collecting of Samples of Real-Emitted Particulate Matter from Different Combustion-Related Sources

2.1.1. Sampling of Particulate Matter Emitted from Residential Solid Fuels Combustion

Samples of particulate matter emitted during residential coal combustion were gravimetrically measured using a specialised probe equipped with a 47 mm diameter filter holder and a 1 kW flue gas pump. The flow of flue gas through the probe was constant and equal as 2.3 $m^3\ h^{-1}$. The fraction of total suspended particles was collected. The particles were sampled on quartz fibre filters (Pallflex®) during combustion of ecopea, bituminous coal, soft wood and culm. Once the PM is collected, the samples were then conditioned for 48 h to stabilize the mass in conditions of constant temperature and humidity. All fuels were combusted three times in domestic heating units (DHU) maintaining similar real conditions in the combustion process. Table 1 summarises the parameters characterizing the domestic heating units used in experiments.

2.1.2. Sampling of Particulate Matter Emitted from Industrial Coal Combustion

As an example of industrial dust samples, the fly ash of the coal combustion process was taken from the 220 MW power unit, equipped with the OP-650 pulverised boiler (Rafako, Poland). Samples were collected from a flue gas duct after the systems of selective catalytic reduction, electrostatic precipitation and wet flue gas desulfurization. Ash particles were collected on 110 mm diameter quartz fibre filters (Whatman® QM-A), applying the automatic gravimetric dust measuring system (ZAM Kęty, Poland) equipped with a heated probe and filtering system, dryer, central control unit, and a regulated sucking pump (4–10 m^3 h^{-1}). The sampling time was 90 or 120 min.

Table 1. The characterisation of domestic heating units utilised during experiments.

Fuel Kind	DHU Type	Sampling Time
Soft wood	Stove, nominal power: 24 kW, efficiency: 83.4%	480–1800 s
Culm	Steel heating boiler with water-cooling water, nominal power 30 kW, efficiency 84%	600 s
Ecopea coal	Central heating unit with a stove dedicated for ecopea coal fuelling	600 s
Bituminous coal	Central heating unit a cast iron stove, nominal power 18 kW, efficiency 77%	600 s

The sampling was carried out according to EN 132841:2001 [29] and PN-Z-04030-7:1994 [30]. Standards regulate the method of measurement of dust mass concentration, which describes, among others, the location demands for measuring points, the size and shape of probes, and the way of sampling in a specific cross section. Furthermore, the sampling and measurement are to be performed in an isokinetic way, since the flue gas velocity in the probe has to be the same as in the flue gas duct.

2.1.3. Sampling of Particulate Matter Emitted from Diesel-Type Engines

Samples of particles emitted from diesel engines were collected basing on the gravimetric filtration method according to the Regulation No. 83 of the Economic Commission for Europe of the United Nations (UN/ECE)–Uniform provisions concerning the approval of vehicles with regard to the emission of pollutants according to engine fuel requirements. The particles were sampled from light and medium duty vehicles on glass fibre filters (Whatmann®) of, respectively, 47 mm and 70 mm in diameter. The glass fibre filters were weighted before and after sampling using a Sartorius weight with an accuracy of 0.0001 mg. The samples were weighted and conditioned at a weighting chamber in constant temperature (22 ± 3 °C) and humidity (45 ± 8%).

Particle samples emitted from a medium duty vehicle were collected using the AVL Smart Sampler 478 equipped with a partial flue gas dilution tunnel on the engine test bed with power brake. AVL Smart Sampler 478 contains a sampling probe, cyclone separator, and filter package for a gravimetric measurement of solid particles. The samples were collected during the European Steady Cycle driving test, which is made up of 13 steps reflecting varied levels of engine load. Each test was 1000 s long. Each time, 54.8 m^3 of flue gas was pumped through the glass fibre filter.

Particles emitted from a light duty vehicle were sampled on a chassis test bed AVL Zoellner 4WD using the constant volume sampling system with a dilution tunnel and a system for gravimetric measurement of particle emission. In order to maintain the real character of studies, the emission tests were conducted to perform both calm urban driving style (low speeds with an average speed at 26 km h^{-1}, low engine loads and low temperature of exhausts) and more aggressive driving style in extra-urban mode with average speed of 69 km h^{-1}.

2.2. Determination of the Content of PM-Bound Chemicals

The batch of samples of particulate matter samples from residential, industrial and automotive sources was analytically measured for the presence of metals and metalloids, including heavy metals like mercury (Hg) and arsenic (As). The content of organic and elemental carbon (OC, EC) and inorganic ions was also measured.

Regarding metals and metalloids the concentration of Cl, K, Ca, Ti, V, Cr, Mn, Fe, Ni, Cu, Zn, Br, Sr, Rb, and Pb was measured using a multifunctional energy dispersive X-ray fluorescence spectrometer according to Samek et al., 2015 and Samek et al., 2016 [31,32]. The QXAS package allowed for quantitative analysis according to Vekemans et al., 1994 [33].

To determine the concentration of PM-bound mercury, a MA-3000 mercury automatic analyzer (NIC, Japan), equipped with an auto sampler, was used. The principle of measurement is based on thermal decomposition, gold amalgamation, and atomic absorption. The method follows the recommendations of US EPA 7473 [34] and ASTM D-6722-01 [35]. The detailed procedures of sample treatment were outlined in previous papers of Authors [14,36].

Carbonaceous mass fraction (OC, EC) was determined using a thermal optical method (Sunset Lab OC/EC aerosol analyzer, Sunset Lab. Inc.) developed for atmospheric samples, using the *quartz.par* temperature protocol and laser in the transmission mode. Details of sample treatment were described in a previous work of Authors [37]. The total carbon (TC) in automotive particulate matter was determined using a carbon analyzer equipped with an infrared radiation detector. The PM sample on a glass fibre filter was burned at 1000 °C under oxygen conditions. The infrared sensor identified the produced CO_2 resulting from the sample combustion. The results were then calculated on the basis of the calibration curve prepared for the TC mass range of 5 to 500 µg. Standard solutions were prepared on the basis of a tartaric acid dilution [38].

The isocratic ion chromatography (IC) was applied to determine the content of inorganic ions as follows: Na^+, K^+, Mg^{2+}, Ca^{2+}, $NH_4{}^+$, $NO_3{}^-$, $NO_2{}^-$, Cl^-, $SO_4{}^{2-}$. IC analysis was performed on an ICS-1100 instrument (Thermo Scientific) equipped with an AS-DV autosampler and ion exchange columns: Ion Pac AS22 (4 × 250 mm) for anions, mobile phase: 4.5 mM Na_2CO_3 + 1.4 mM $NaHCO_3$; CS16 (5 × 250 mm) for cations, mobile phase: 12 mM MSA. After electrochemical suppression (AERS 500 (4 mm) and CERS 500 (4 mm) suppressors): quantification was performed with a conductivity detector. The injection volume was 25 µL and the flow rate was 1.2 mL min^{-1}. The details of methodology applied was previously described in Szramowiat-Sala et al., 2019 and Pacura et al., 2022 [12,39].

3. Results and Discussion

3.1. Real-Emission of Particulate Matter from Different Combustion-Related Sources

Figure 1 presents the results of gravimetric analysis and mass reconstruction of particulate matter emitted from seven combustion-related sources. WOOD refers to soft wood combustion in a DHU, CULM–to culm combustion in a DHU, ECOPEA–to ecopea coal combustion in a DHU. $COAL_{(In)}$–to industrial bituminous coal combustion, COAL–to bituminous coal combustion in a DHU, LDDV–to low-duty diesel vehicles and MDDV–to medium-duty diesel vehicles.

The gravimetric measurements of mass concentration of particulate matter real-emitted from combustion-related sources demonstrated that the highest PM emission in flue gas was reported for bituminous coal combustion in a domestic heating unit and was equal to 464.7 mg m^{-3}. The emission of PM from combustion of other solid fuels was several times lower and complied with a decreasing trend CULM > WOOD > $COAL_{(In)}$ > ECOPEA referring to concentrations equal to: 36.7, 20.9, 5.9 and 5.3 mg m^{-3}, respectively. The recorded mass concentration of particulate matter resulting from industrial coal combustion adheres to the thresholds outlined in Best Available Techniques conclusions [40], which establish a PM emission range of 5–50 mg per normal m^3 of flue gases. It is clear that the employed electrostatic precipitator, utilized within the power plant where PM samples were gathered, effectively eliminated the dust produced during the combustion process, contributing to the release of cleaner flue gases into the atmosphere. The release of particulate matter from automotive sources exhibited notably lower figures when contrasted with the combustion of residential and industrial fuels. It was recorded at 592.5 µg m^{-3} for low-duty and 101.9 µg m^{-3} for medium-duty diesel vehicles, which translates to emission rates of 0.0003 and 0.0005 g km^{-1}, respectively. These findings align with, or marginally surpass in the case of MDDV, the PM emission limits stipulated by EURO 6 regulations, which have been established at 0.0045 g km^{-1}.

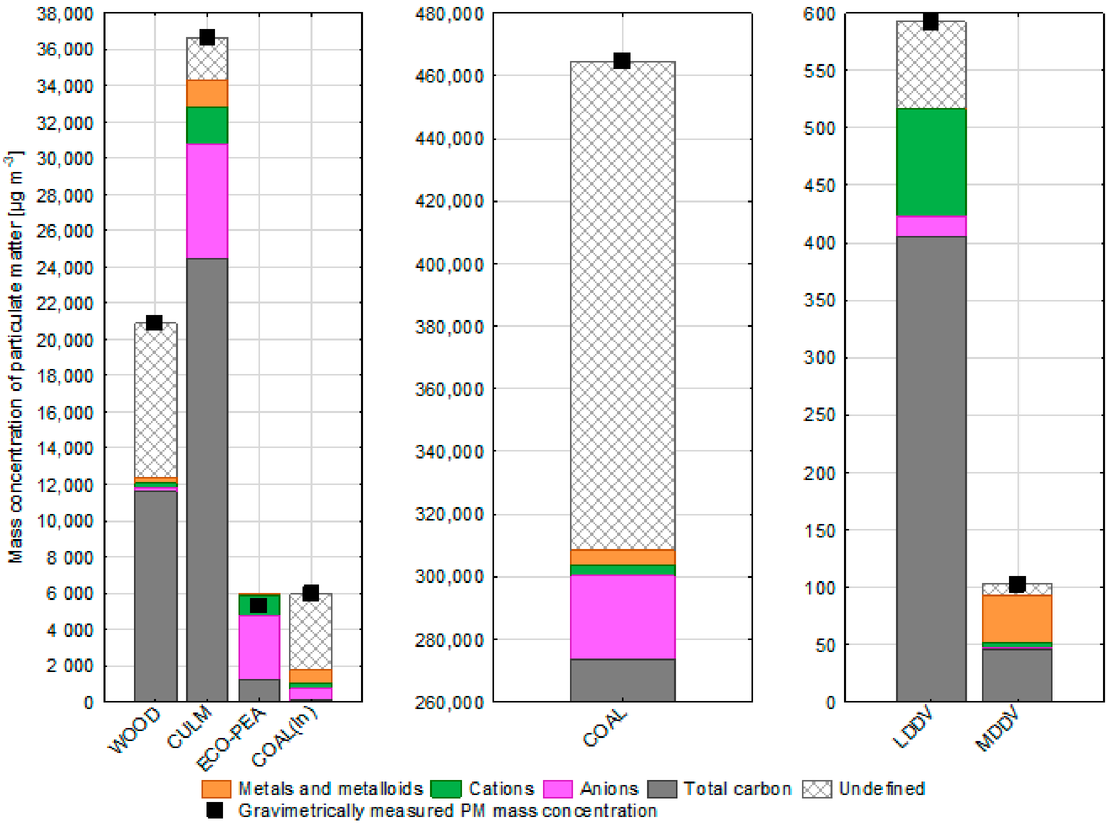

Figure 1. Mass concentration of real-emitted particulate matter from different combustion-related sources (columns—PM mass reconstruction on the base of PM-bound components mass; ■—the gravimetrically measured mass of PM).

The analysis of particle sizes within particulate matter originating from industrial combustion revealed that the particles contained 22.9% within the $PM_{2.5}$ fraction and 74.9% within the PM_{10} fraction [14]. This distribution might be influenced by chemical and physical reactions occurring within fume gas ducts, leading to an alteration in particle dimensions. Similar findings have been reported by other researchers who observed that particle size distribution resulting from the combustion of solid fuels typically follows a bimodal pattern. In the case of coal combustion, it generates a greater proportion of coarse particles compared to fine particles [41,42]. Biomass combustion, conversely, often produces a higher quantity of fine particles compared to coal [43]. However, following carbonization or torrefaction pretreatment, emissions of fine particles typically experience a substantial reduction [44]. The size distribution of particles of automotive origin has been already widely studied. It was reported that the majority of PM from diesel-fuelled vehicles is in the nanoparticle range [45] with peak concentrations within the range 16–124 nm [46–48]. This reinforces the fact that individuals are primarily exposed to the finer fractions of particulate matter derived from combustion-related sources, which present greater health hazards than their coarser counterparts.

The PM samples collected during the combustion of various fuels underwent detailed analytical treatment, enabling the determination of the major chemical constituents present within the particulate matter. Figure 1 illustrates a column chart that depicts the reconstruction of PM mass based on the summation of masses attributed to analytically measured PM-associated substances, which encompass carbonaceous compounds like organic and elemental carbon, as well as metals, metalloids, and inorganic ions, comprising both cations and anions. The category termed “Undefined” was calculated as the difference between the mass of gravimetrically measured PM and the cumulative mass of PM components determined analytically. This represents the portion of PM that eluded specification during laboratory analysis. For particulate matter stemming from wood, culm, and coal combustion in domestic heating units, as well as from diesel-fuelled vehicles, the undefined fraction did not surpass 15% of the total PM mass. In contrast, within PM generated from industrial coal combustion, the undefined fraction dominated, accounting for over 60% of the PM. This can be attributed to the substantial contribution of inorganic PM components, often characterized by their hygroscopic nature. It is also plausible that certain constituents of PM, such as polycyclic aromatic hydrocarbons found in the organic matter, mercury bound to PM, nitric ions, ammonium ions, and sulphate ions, might have evaporated during sample preparation or transfer. The accuracy and ultimate outcomes of PM measurements can also be influenced by the chosen methodology. Nussbaumer et al., 2008 [49] underscore that the selection of sampling methods warrants meticulous consideration of the physical and chemical attributes of the PM, thereby minimizing measurement inaccuracies. To mitigate errors, it is recommended that particulate matter samples be collected through pre-dilution techniques, which prevent chemical condensation that might otherwise lead to an overestimation of PM mass concentrations. However, the authors' intent in this context was to characterize the real risk posed by exposure to combustion-related particulate matter in its natural state.

Notably, for particulate matter originating from combustion of ecopea coal, the reconstructed mass exceeded the gravimetrically measured PM mass. This discrepancy could be attributed to a potential overestimation in the analytical data due to the relatively low masses of the PM samples being analyzed. The detailed discussion regarding PM-bound components is presented in 3.2–3.4 chapters.

3.2. PM-Bound Carbonaceous Compounds

The predominant share of particulate matter originating from the combustion of different fuels is attributed to carbonaceous compounds. This is particularly pronounced in the case of softwood combustion (55.5%), culm combustion (66.7%), and bituminous coal combustion (58.9%) within residential heating units (Figure 1). Specifically, organic carbon constituted 54% of the total carbon content derived from softwood, 81% from culm, and a substantial 96% from bituminous coal. Conversely, for particles stemming from the combustion of ecopea coal, carbonaceous compounds made up 23% of PM, with a cumulative concentration as high as 1230 $\mu g\ m^{-3}$. This concentration is notably lower when compared to total carbon concentrations arising from softwood combustion by a factor of 9, from culm combustion by a factor of 20, and from bituminous coal combustion in domestic heating units by a substantial factor of 223.

Conversely, industrial combustion of bituminous coal exhibited the lowest levels of carbonaceous compounds, accounting for a mere 1.6% of PM mass (as shown in Figure 1). The concentrations of organic and elemental carbon were correspondingly low at 72.1 and 20.1 $\mu g\ m^{-3}$, respectively. This diminished presence of carbonaceous compounds in the PM emissions from power plants likely stems from the effective operation of exhaust aftertreatment systems within the flue gas ducts, which efficiently remove these compounds from the particulate matter, leaving behind mineral and metallic constituents.

In the realm of mobile sources, the mass of total carbon made up 45% of particulate matter emissions from medium-duty diesel vehicles (MDDV) and a more significant 70% from light-duty diesel vehicles (LDDV). This aligns with the findings of He et al.'s study in 2017, indicating that elemental carbon typically constitutes up to 56% of the overall carbonaceous content within particulate matter originating from diesel sources. Furthermore, according to the mentioned study, the remaining portion, approximately 44%, can be attributed to the low-volatility organic fraction (derived from fuel and lubricating oil) and the high-volatility organic fraction (associated with unconsumed fuels) [48].

To comprehensively characterize particulate matter originating from diverse combustion-related sources, the analysis incorporated the computation of mass ratios between organic carbon and elemental carbon (OC/EC). This parameter serves as a valuable indicator of the carbonaceous composition within the particulate matter. The highest OC/EC value of 24.0 was identified in PM derived from residential combustion of bituminous coal. This heightened ratio suggests a prevalence of organic carbon over elemental carbon in this context. In the case of domestic ecopea coal combustion, an OC/EC value of 13.2 was recorded, reflecting a substantial organic carbon presence relative to elemental carbon. Notably lower OC/EC values were observed for culm combustion in domestic heating units, registering at 4.3. Similarly, industrial coal combustion in power plants yielded a relatively modest OC/EC value of 3.6. For particulate matter arising from the combustion of softwood, an OC/EC value of 1.2 was noted. Interestingly, this value is notably lower—3.5 times so—compared to the value proposed by Sillanpää et al., 2006 [50], which stood at 4.15. It is pertinent to mention that Sillanpää et al., 2006 study reported a substantially low OC/EC ratio of 0.8 for diesel vehicles. Conversely, significantly higher OC/EC ratios were documented for domestic fuel combustion.

The presence of a substantial amount of organic carbon relative to elemental carbon could indicate that the combustion processes are not operating optimally, which in turn can lead to the emission of harmful and potentially toxic substances. This underscores the importance of efficient combustion techniques, proper fuel preparation, and adequate air supply to minimize the formation of these hazardous compounds. The pronounced prevalence of organic carbon over elemental carbon within the particulate matter composition can likely be attributed to incomplete combustion processes. This phenomenon gives rise to the formation of potentially hazardous compounds, such as polycyclic aromatic hydrocarbons (PAHs). Incomplete combustion, characterized by insufficient oxygen availability, tends to produce a higher proportion of organic carbonaceous compounds. These compounds are formed when complex hydrocarbons in the fuel are not completely broken down into simpler components like carbon dioxide. Instead, they undergo partial breakdown, leading to the creation of compounds like PAHs. These compounds are of concern due to their potential to pose health risks. PAHs are known to have carcinogenic properties and are associated with various respiratory and cardiovascular ailments when inhaled [12,39].

3.3. PM-Bound Inorganic Ions

The proportion of anions within the particulate matter exhibited variations contingent on the specific fuel subjected to combustion. The particulate matter stemming from softwood combustion exhibited the lowest anion content, constituting a mere 1.2% of particulate matter. A slightly elevated concentration of anions, 5.7%, was recorded for particulate matter resulting from the combustion of bituminous coal in domestic heating units (DHUs). This 5.7% equates to 26,643 $\mu g\ m^{-3}$, a concentration fourfold higher than the summed anion concentration from culm combustion. In the latter case, anions contributed to 17.3% of the particulate matter’s mass. The composition of PM originating from industrial coal burning revealed anionic contributions of 11% of the PM mass. A notably distinct pattern emerged in the case of ecopea combustion within DHUs, where anions took the most substantial share, accounting for a striking 67.5% of the mass (Figure 1).

The concentration of inorganic ions within the particulate matter exhibited distinct patterns, with the highest concentrations being observed for chloride ions (Cl^-) and sulphate ions (SO_4^{2-}). An orderly examination of these findings reveals several trends (Figure 2A):

- Within particulate matter stemming from softwood combustion, sulphate ions took the lead, contributing a significant 60% of the overall anion mass. Chloride ions, though slightly lower, still held substantial prominence, contributing 28% to the anion mass.
- The presence of fluorine ions (F^-) was identified in particulate matter arising both from residential coal combustion and the industrial process of coal burning. In the former, the concentration of fluorine ions with a concentration of 500 $\mu g\ m^{-3}$ accounted for 1.5% of the total anion mass, while in the latter, it rose to 25%. The similar contribution (21% and 24%) of F^- mass was also noticed for low-duty and medium-duty diesel vehicles, respectively.
- In the context of residential coal combustion, chlorine ions dominated the anion composition, contributing a substantial 95% of the anion mass. In coal burning in a DHU, sulphates shared a smaller proportion, comprising 2% of the anion mass.

- Ecopea coal combustion and bituminous coal combustion in power plants displayed the lowest contributions of chloride ions. In particulate matter from ecopea coal combustion, chlorides contributed a mere 25% of the anion mass. Meanwhile, the anions balance leaned heavily towards sulphate ions, making up almost 100% of the anion mass.
- Chlorines and sulphates contributed in 28% and 70%, respectively, to anions fractions of particulate matter from culm combustion.
- Nitrates were observed only in PM derived from medium-duty diesel vehicles.

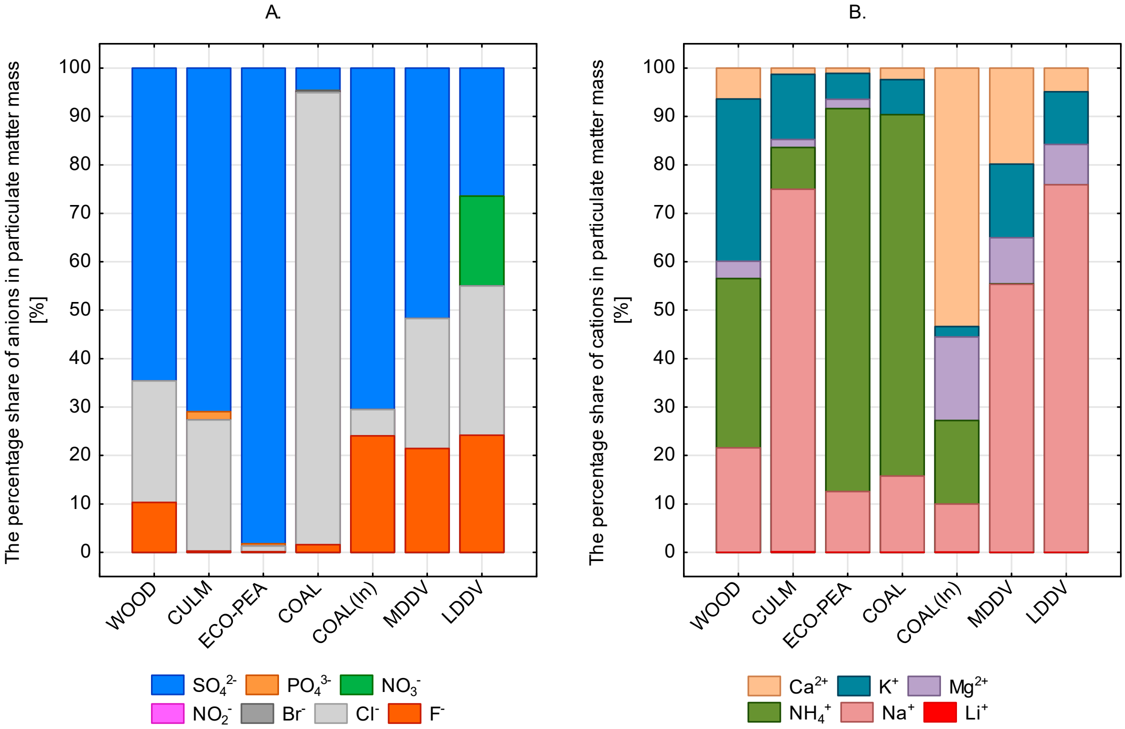

Figure 2. The share of inorganic ions ((**A**). anions, (**B**). cations) in particulate matter real-emitted from different combustion-related sources.

The distribution of cations within the analyzed particulate matter exhibited distinct variations contingent on the combusted fuel (Figure 2B). The findings can be systematically elucidated as follows:

- The cumulative concentration of cations in particulate matter from residential coal combustion amounted to 3.600 $\mu g\ m^{-3}$, while from ecopea coal burning, it stood at 1.050 $\mu g\ m^{-3}$. These figures contributed to 0.8% and 20.0% of the particulate matter's mass, respectively. Notably, cation mass originating from combustion exceeded that from ecopea coal burning by a factor of 2.0, constituting 6% of PM mass.
- The lowest concentrations of cations were registered in particles emitted from softwood combustion (200 $\mu g\ m^{-3}$) and bituminous coal combustion in power plants (346 $\mu g\ m^{-3}$).
- Inorganic ions contributed 2% of PM mass for light-duty diesel vehicles (LDDV) and 8% for medium-duty diesel vehicles (MDDV). Notably, among the cations, sodium cations held the highest contribution, comprising 76% of the cation mass for LDDV and 55% for MDDV. Potassium and calcium also held substantial proportions within this ionic balance.
- In PM from coal and ecopea coal combustion in DHUs, ammonium ions (NH_4^+) were predominant, contributing to over 80% of the cation mass. Lower NH_4^+ content was observed in PM from culm (10%), softwood (38%), and power plant emissions (20%).
- In the case of softwood combustion, potassium cations (K^+) exhibited a prevalence similar to that of ammonium ions. Sodium cations (Na^+) shared about 20% of PM

originating from softwood. Culm combustion particles were dominated by sodium ions (75%), while the contributions of K^+ and NH_4^+ were notably lower at 12% and 10%, respectively. In PM from the power plant, cation contributions differed, with the majority of the mass comprising mineral components such as Ca^{2+} (55%), Mg^{2+} (20%), NH_4^+ (19%), and Na^+ (10%).

These findings corroborate existing literature, such as the study by Popovicheva et al. in 2014 [51], reinforcing the consistency of the results obtained and enhancing the broader understanding of cation distribution across various combustion sources.

The relationship between anions and cations, characterized by the equivalent concentrations ratio of anion to cation (A/K), exhibited distinct behaviours across various combustion scenarios. Notably, only in the case of industrial coal combustion did the proportions of anions and cations achieve equilibrium, indicated by an A/K value of 0.95. In the remaining instances involving wood, culm, ecopea, coal, medium-duty diesel vehicles (MDDV), and light-duty diesel vehicles (LDDV), the A/K ratios displayed specific values of 0.7, 1.6, 1.3, 4.0, 0.16, and 0.06, respectively. The most noteworthy elevation in A/K ratio was observed for coal burnt in domestic heating units, registering a value of 4.0. This substantial value stemmed from an excess of anions, particularly chloride ions. It is reasonable to assume that these chlorides are predominantly bound to NH_4^+ and Na^+. Calculating this surplus, the mass concentration of chloride excess reached 18,567 $\mu g\ m^{-3}$. The intriguing aspect was the surprisingly low A/K ratios for mobile sources, underscoring a pronounced excess of cation concentration within particulate matter. This deviation from balance could be attributed to the presence of cations in insoluble forms, which limits their ability to maintain equilibrium with anions. he varying A/K ratios underline the intricate chemistry of ion interactions and solubility patterns within emitted particulate matter. The intricate interplay between anions and cations in particulate matter highlights the complex chemistry occurring during combustion processes. This chemistry is probably influenced by factors such as fuel type, combustion temperature, and reaction kinetics.

3.4. PM-Bound Metals and Metalloids

Among the various components of particulate matter, metals and metalloids occupied the lowest share, as depicted in Figure 1. The analysis of particulate emissions from coal combustion indicated that the cumulative mass of the analyzed elements constituted less than 1% of the total PM mass, despite their collective concentration being 4400 $\mu g\ m^{-3}$. Conversely, for wood, ecopea, and culm combustion, the contribution of metal and metalloid mass ranged from 1.7% to 3.8%, corresponding to total concentrations of 500 $\mu g\ m^{-3}$, 1400 $\mu g\ m^{-3}$, and 100 $\mu g\ m^{-3}$, respectively. Intriguingly, the highest elemental mass contribution to the overall PM mass was observed in the case of PM from industrial coal burning, exceeding 11%. The total concentration of these elements in this context was measured at 670 $\mu g\ m^{-3}$.

Delving into stationary sources, potassium (K) emerged as the dominant element in terms of mass contribution (Figure 3). This prominence was evidenced by its mass share of 60%, 59%, and 35% in the PM originating from wood, ecopea coal, and culm combustion, respectively. In the realm of industrial and domestic coal combustion, K's mass contribution was 18% and 2%, respectively. A noteworthy finding was the prevalence of chloride in the elemental composition of PM from domestic coal combustion. This observation aligns with the ionic composition, reinforcing the connection between cations and anions within particulate emissions. In summary, the analysis underscores the relatively low contribution of metals and metalloids to the overall mass of particulate matter. However, their specific contributions and compositions vary widely across different combustion-related sources, emphasizing the intricate interplay between combustion conditions, fuel characteristics, and the resulting chemical interactions.

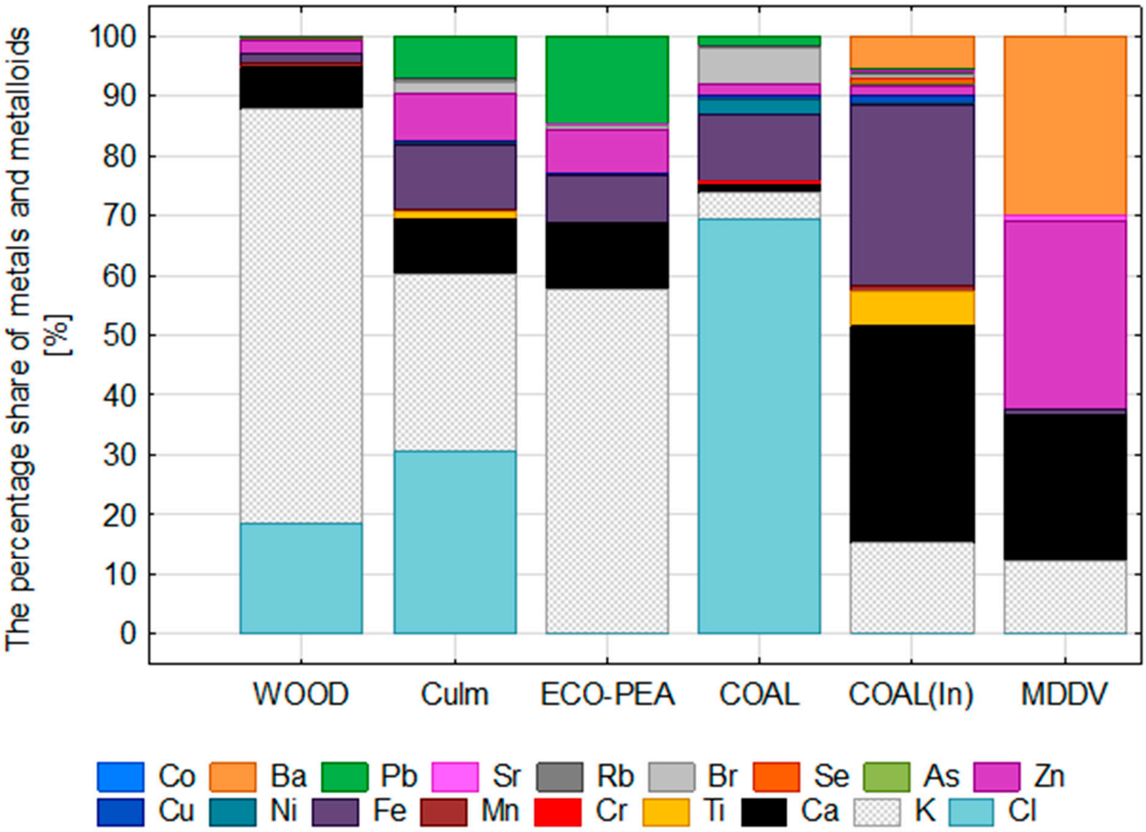

Figure 3. The share of metals and metalloids in particulate matter real-emitted from different combustion-related sources.

The elemental fraction of particulate matter comprised the residual portion and was characterized by the presence of iron (10%), nickel, calcium, barium, lead, and copper. Analogously to the ionic composition, in the context of particulate emissions resulting from industrial coal combustion, the elemental fraction was largely dominated by mineral components. Notably, calcium constituted around 30% of the total metallic mass, iron accounted for another 30%, and potassium contributed 18%. The remaining segment of the elemental fraction encompassed titanium, barium, copper, chloride, selenium, and manganese, as illustrated in Figure 3.

Chloride held precedence in particulate emissions from wood combustion, constituting 18.6% of the metals and metalloids mass together. Similarly, the combustion of culm demonstrated a significant chloride presence, with a share of 30.7% in the metals and metalloids mass. In the case of culm and ecopea coal combustion, nearly 37.0% of the elemental fraction was attributed to lead, zinc, iron, calcium, and bromide.

Shifting to medium-duty diesel vehicles (MDDV), potassium and calcium emerged as dominant elements. Barium and zinc shared 29.8% and 31.2% of the mass of elemental fraction, respectively (Figure 3). However, for particulate matter originating from light-duty diesel vehicles (LDDV), the analysis of elemental composition remained unattainable due to insufficient analytical material. Nevertheless, by comparing the chemical composition presented in Figure 1, it can be surmised that the distribution of metals and metalloids was relatively similar, potentially accounting for 20–30% of the composition. Notably, crustal metals predominated within this elemental fraction. Metals found in particulate matter (PM) from diesel-fuelled vehicles typically originate from a combination of sources, which can be broadly categorized into two main groups: engine wear and exhaust emissions and external sources and road dust. The combustion of diesel fuel in vehicle engines produces exhaust emissions that contain trace amounts of metals. These metals can come from various sources within the engine, such as lubricating oils, fuel additives, and wear of engine components like pistons, cylinders, and valves. These metal-containing particles can be emitted directly into the exhaust as a result of friction and high-temperature processes occurring within the engine. Vehicles on the road can stir up road dust, which contains a mix of particulates from tire and brake wear, road surface abrasion, and other sources. This road dust can become suspended in the air and contribute to the particulate matter emissions from vehicles. The metals present in road dust can include those originating from wear and tear of road surfaces, tire and brake components, as well as pollutants from surrounding urban environments [10].

In conclusion, the elemental fraction of particulate matter showcases a diverse composition influenced by the specific combustion process and fuel source. The prevalence of certain elements and metals underscores the intricate interplay of combustion conditions, mineral content, and chemical reactions, offering valuable insights into the origin and characteristics of particulate emissions.

Figure 4 illustrates the average concentrations of mercury and arsenic within particulate matter generated through the combustion of solid fuels in both residential and industrial settings. The presence of mercury within the particulate matter was evident across all fuels examined with an exception of ecopea coal combustion. Notably, the most substantial emission was recorded in the context of domestic coal combustion, reaching a level of 380 ng m^{-3}. Conversely, the lowest Hg concentration was identified in the case of ecopea coal combustion, measuring a mere 25 pg m^{-3}. Impressively, industrial coal combustion and domestic coal burning emitted mercury concentrations that were a thousandfold greater than those of ecopea coal combustion.

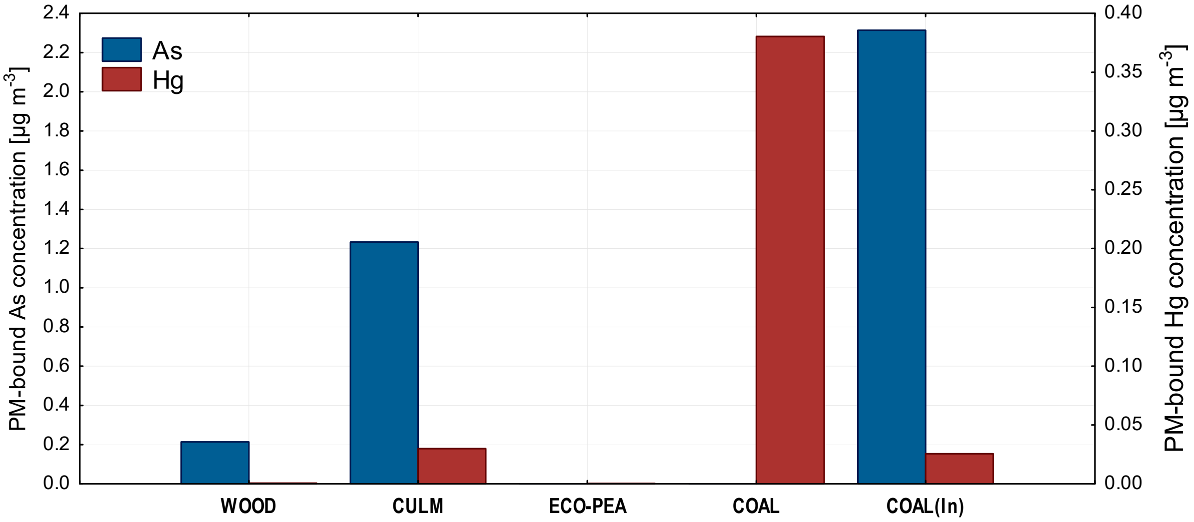

Figure 4. Concentration of PM-bound arsenic and mercury from stationary combustion sources.

In the scenario of arsenic, its occurrence was exclusive to wood, culm, and industrial coal combustion. Arsenic concentrations spanned from 0.2 to 2.3 μg m^{-3}. Noteworthy distinctions in the particulate matter composition emerged between coal combustion in industrial and domestic settings. In industrial coal burning, where exhaust aftertreatment technologies are employed, particulate matter was predominantly comprised of mineral constituents. Consequently, arsenic demonstrated greater prominence in PM originating from industrial coal combustion than in domestic heating units. From this observation, it can be deduced that arsenic predominantly associates with the mineral fraction of particulate matter. Conversely, mercury exhibited a stronger affinity for the carbonaceous fraction of PM what could be confirmed by a constant Hg-to-OC ratio for PM of coal origin with standard deviation 0.55.

In essence, the findings underscore the distinct behaviours of mercury and arsenic within particulate matter stemming from solid fuel combustion, shedding light on their specific interactions with different components of the particulate emissions.

4. Identification of Characteristic PM-Bound Chemical for Different Combustion-Related Sources

The paper discusses the real-emission of particulate matter from various combustion-related sources and provides information about the components of particulate matter emitted from these sources. On the base on obtained results the following information may be extracted to shortly characterize the specific emission sources:

Residential combustion of coal:

- High PM emission.
- Dominance of carbonaceous compounds, including organic carbon and elemental carbon, contributing to a significant portion of PM mass.
- Anion contribution around 5.7%, with chloride ions being prominent.
- Low contribution of metals and metalloids (<1% of PM mass), but specific elements like lead, zinc, iron, calcium, and bromide are present.

Residential combustion of culm:

- Lower PM emission compared to coal combustion.
- Predominance of carbonaceous compounds, with organic carbon constituting a major fraction.
- Anion contribution around 17.3%, with chloride ions being significant.
- Relatively higher contribution of metals and metalloids (1.7–3.8% of PM mass), including lead, zinc, iron, calcium, and bromide.

Residential combustion of ecopea:

- Lower PM emission compared to coal combustion.
- Presence of carbonaceous compounds, but less significant compared to coal and culm combustion.
- High anion contribution (67.5% of PM mass), predominantly sulphate ions.
- Moderate contribution of metals and metalloids (1.7–3.8% of PM mass), including lead, zinc, iron, calcium, and bromide.

Residential combustion of wood:

- Moderate PM emission.
- Dominance of carbonaceous compounds, with a higher contribution of organic carbon.
- Anion contribution around 1.2%, mainly sulphate ions.
- Moderate contribution of metals and metalloids (1.7% of PM mass), including lead, zinc, iron, calcium, and bromide.

Industrial coal combustion:

- Significant PM emission, meeting emission standards due to effective exhaust aftertreatment.
- Low presence of carbonaceous compounds due to efficient removal mechanisms.
- Anion contribution around 11%, with sulphate ions being prominent.
- Higher contribution of metals and metalloids (>11% of PM mass), including calcium, iron, potassium, titanium, barium, copper, chloride, selenium, and manganese.

Medium-Duty Diesel Vehicles (MDDV):

- Lower PM emission compared to solid fuel combustion.
- Presence of carbonaceous compounds, with both organic carbon and elemental carbon contributing.
- Anion contribution around 8%, dominated by chloride ions.
- Contribution of metals and metalloids (2% of PM mass), with potassium, calcium, barium, and zinc being dominant.

Light-Duty Diesel Vehicles (LDDV):

- Lower PM emission compared to solid fuel combustion.
- Presence of carbonaceous compounds, with both organic carbon and elemental carbon contributing.
- Anion contribution around 2%, mainly chloride ions.

These conclusions will serve for the optimisation of the macro-tracer model serving as a PM source apportionment technique and will be the subject of future work od Authors.

5. Conclusions

The chemical characterisation of particulate matter has been demonstrated to be diverse and contingent upon the source responsible for its generation. The study analyzed the composition of three principal categories of PM components: the carbonaceous fraction, elemental fraction, and ionic fraction. The contribution of specific components to each fraction exhibited distinct characteristics for each emission source. Notably, marked disparities emerged, particularly in cases of coal combustion within residential and industrial contexts.

The application of exhaust after treatment processes in coal-fired power plants resulted in the elimination of the carbonaceous fraction, while mineral components endured within the particulate matter. Industrial coal combustion exhibited a distinctive presence of arsenic as a notable element. Domestic coal emissions were marked by the presence of organic carbon, chlorides, and mercury. In the case of ecopea coal, the identification of sulphate ions was distinctive. Organic matter-rich fuels such as culm, wood, and diesel yielded specific organic compounds, likely representative of anhydrosugars or nitric and oxygenated derivatives of polycyclic aromatic hydrocarbons.

The integration of the findings into this study can facilitate the refinement of macro-tracers for source apportionment of PM. To enhance the differentiation of coal-related emission sources, further research is recommended, delving into the concentration of PM-bound microcomponents such as polycyclic aromatic hydrocarbons or their nitric- and oxygenated derivatives. Additionally, given the elevated toxicity and carcinogenicity index associated with organic PM microcomponents, a more comprehensive investigation of their actual emission ratios is warranted.

Nonetheless, the experiments' outcomes affirm the intricate nature of PM generation from distinct sources. The chemical characterization of PM is closely intertwined with the mechanical and thermodynamic conditions inherent in combustion processes, whether in stationary devices or automotive vehicles. Monitoring the particle generation process holds the key to comprehending the destiny of particulate matter and averting its release into the atmosphere. These inquiries necessitate extensive exploration and remain central to our ongoing research endeavors.

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