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An overview of some challenges in the studies in the emission of particulate matter

A Korzeniewska¹, K Szramowiat^{1,*}, J Gołaś¹

¹AGH University of Science and Technology, Faculty of Energy and Fuels, Kraków, Poland

E-mail: katarzyna.szramowiat@agh.edu.pl

Abstract. Studies of particulate matter (PM) emission from solid fuel combustion are important due to the fact that PM has a negative impact on the environment and on human health. The combustion of solid fuels such as coal and biomass for the generation of heat and electricity is one of the principal contributors to PM emission. Coal fired boilers are widely used in power plants due to their low cost despite the fact that coal combustion produces significant amounts of pollutants. A large fraction of the emission of anthropogenic PM and black carbon comes from the household coal combustion for heating and cooking. Residential coal combustion has significantly high emission factors of PM, elemental carbon, and organic carbon, due to incomplete combustion and the lack of an installation of an air pollution control. During high PM pollutant episodes in winter, coal combustion is considered the largest anthropogenic source, especially for organic aerosols. This work supports the synthesis of recent studies on organic pollutants emitted during combustion processes. The paper presents the forms of organics in solid phase, as condensed on the surface of the PM.

1. Introduction

Particulate matter (PM) is composed of hundreds or even thousands of compounds [1]. PM is a complex mixture of elemental and organic carbon, sulfates, nitrates, ammonium, and metals. It originates from both the natural (involving sea-salt particles, windblown sand, volcanic ash) and anthropogenic sources (industrial processes, traffic sources, fuel combustion) [2]. It is important to obtain a clear understanding of the composition of atmospheric PM as some compounds or species such as benzo(a)pyrene pose health threats. Some species can be used as powerful tracers for sources. Such information is particularly important for PM_{2.5} source apportionment in order to lower PM_{2.5} concentration in ambient air and protect human health [1].

Particle pollution includes inhalable coarse particles, fine particles and ultra-fine particles. Coarse particles are generally defined as those having an aerodynamic diameter larger than 2.5 µm (PM_{2.5}) and smaller than 10 µm (PM₁₀). Fine particles are those having an aerodynamic diameter less than 2.5 µm, and ultra-fine particles are those less than 100 nm in diameter.

Combustion processes may be classified into area or point sources, stationary or mobile sources. Mobile sources are mainly motor vehicles, but they also include aircraft and boats as well as small sources such as lawnmowers. Stationary sources are industrial plants, power plants, refineries, etc. The relative and absolute importance of these sources varies. It is a function of source strength, co-occurring with other PM sources and population density in the vicinity of the sources.



Combustion processes result in generation of a large number of particle products that create health and environmental risks. Of particular importance are the very small particles that are emitted in large quantities from all the combustion processes, and that have been shown to be potentially more significant in terms of their impact on health than larger particles. The following combustion processes that have the most significant relative contribution to air pollution and which result in exposures and risks to large populations will be discussed in this paper: road transport, power plants and industrial combustion classified as industrial facilities, small combustion (domestic, commercial, public and agricultural combustion processes), and vegetation burning [3].

2. The emission of particulate matter from combustion processes

To address climate change, countries adopted the Paris agreement at COP 21 in Paris in 2015. In order to reduce the emission of greenhouse gases, it led to the increase in the use of wood-burning stoves and boilers particularly in Europe. The use of solid biofuel has been the fastest growing energy source in the EU. According to that, in the EU a proposal to bring much tighter legislation by 2022 (Eco-design) for solid fuel local space heaters with PM emission varying according to fuel type was made [4]. The biofuel combustion led to the increase in related emissions, which especially contribute to the PM burden of the atmosphere. In wintertime, wood burning has a large contribution to air pollution even in big cities like Berlin, Paris or Kraków. The wood combustion has a share comparable to that from traffic sources.

According to the reports, the dynamics of changes in the structure of the global fuel and energy balance indicates continuing dependence on fossil fuels as a primary energy source. The data presented in "Monthly reports on the functioning of the National Power System and Balancing Market" shows that, electricity production from hard coal has decreased in recent years from 61.6% in 2007 to 53.9% in 2015. The decrease is caused by increased lignite usage, which is less expensive than hard coal [5].

2.1. Stationary processes

Among stationary anthropogenic sources one may distinguish local furnaces, incineration plants, agricultural activities, logging and mining and chemical production. The chemical composition of the particles emitted during domestic combustion is closely related to the combustion conditions, and thus to the concentrations and size distributions. Studies showed that unsatisfactory combustion conditions cause generation of particles mostly consisting of organic material, and that particularly under sub-stoichiometric conditions and at low temperatures the particles from a wood stove mainly consist of organic carbon. However, at higher temperatures, the aerosol composition contains less carbon and larger fractions of potassium, chlorine and sulfur [6].

The combustion of solid fuels such as coal and biomass for heat and electricity generation is one of the principal contributors to PM emissions. For example, inefficient combustion in cooking stoves generates products of incomplete combustion, leading to the formation of gases, volatile organic compounds (VOC), and PM [7]. The evaluation of particles emission factors proved that the energy production in domestic devices is one of the major sources of atmospheric fine particles, particularly in Europe.

Coal-fired boilers are widely used in power plants due to their low cost and to the abundance of this fuel despite the fact that coal combustion produces significant amounts of pollutants. As far as biomass is concerned, the residential wood combustion mainly contributes to local air pollution with emissions of various gaseous compounds and PM [8].

Particles generated by the burning of biomass, under poor combustion conditions, consist mainly of carbonaceous compounds, mostly organic carbon and smaller amounts of elemental carbon, while during efficient combustion conditions, they are mainly formed by ash-related material.

One observed a significant difference in the chemical composition of PM₁₀ emissions from manually and automatically fired systems. It was verified that during the combustion processes occurring in logwood stoves caused the emission of high amounts of carbonaceous material bound

with PM, while particulate emissions from automatically fired systems (pellet stove and boiler) consisted mainly of inorganic potassium salts [9]. Experiments were also carried out using a high efficiency pellet boiler and one observed that the PM resulting from efficient combustion conditions is mainly formed by inorganic material [10]. Others have reported that particulate emissions are almost entirely composed of ash-related material during efficient combustion conditions [11].

2.2. Mobile processes

Traffic is an important source of air pollution worldwide. The combustion of both diesel and petrol fuels produces combustion-derived fine PM (aerodynamic diameter $< 2.5 \mu\text{m}$), which vary between each other in terms of chemical composition [12]. It was observed that gasoline vehicle emissions have high concentrations of the OC fractions, while diesel vehicle emissions have high concentration of EC as it contained lots of high-temperature component of EC particles [13].

Emission from motor vehicles is an important source of primary PM in urban environments. Emitted pollutants including black carbon, toxic components, and precursors of secondary PM are of great concern. Vehicular emission in megacities can contribute to almost 20-30% of PM_{2.5} [14]. One observed that the emission rates for ultrafine and fine particles for heavy duty diesel vehicles (HDDVs) are one order of magnitude higher than LDGVs. Others have reported 4-times higher diesel emission factors (EFs) compared to gasoline EFs in a tunnel environment. Vehicles are also a major source of n-alkanes and diesel engines are known to emit more n-alkanes compared to gasoline engines [15]. However, traffic-related PM is not only associated with direct automobile exhaust emissions and gas-to-particle conversion processes, but also with tire and brake wear, asphalt, engine oil and re-suspension of road dust. An improved understanding of the chemical characteristics of PM of traffic origin and the identification of their specific sources is needed to reduce of air pollution [16].

Diesel engine exhausts are multi-component mixtures of several hundred chemical compounds, resulting from imperfect burning of diesel oil as well as the modifiers and impurities contained therein. These undesirable combustion products are released into the atmosphere in the form of gases and vapors as well as in the form of particles.

Legislations from all over the world set limits to PM emissions from diesel engines. These regulations are mostly achieved by diesel particulate filters (DPF) [17]. The EURO 6 regulations introduced a PM emission limit as well as PN –particulate number. So far, diesel engines are believed to be the main cause of particulate emissions. The engine industry handled this problem by introducing solid particle filters.

However, it appears that petrol engines are also a source of particulates, especially as far as engines with direct petrol injection are concerned. The PM emitted in these processes is considerably smaller in terms of the aerodynamic diameter dimension, and it is much greater numerically than in the case of emissions from compression-ignition engines.

On the basis of the experience of the chemical characteristics of the PM and the available literature, it has now been pointed out that the emission of PM as a result of combustion processes in petrol engines is a significant problem for engine builders.

Traffic-related PM_{2.5} consists of a complex chemical mixture including elemental carbon (EC) and organic carbon (OC) with diverse functional groups, as well as small amounts of water-soluble ions, trace elements, and water. Solar radiation can be effectively absorbed by EC, which affects global climate. While compounds (some semi-volatile hydrocarbons including polycyclic aromatic hydrocarbons (PAHs)) included in the OC fraction are suspected human carcinogens. Traffic-related PM_{2.5} contains redox-active trace elements such as Ni, Cr, Co, and As that contribute to both carcinogenic and non-carcinogenic risk to individuals exposed to outdoor air pollution [16].

On the surface of solid particles, organic and inorganic compounds, mainly sulphates, are adsorbed. PM consists in 15-45% of organic soluble fraction. This organic fraction is mostly composed of:

- paraffins: C₅ - C₄₀ aliphatic hydrocarbon mixture,
- aromatics: a mixture of aromatic hydrocarbons, polycyclic aromatic hydrocarbons and their derivatives, acetates, aldehydes,

- acidics: a mixture of phenol and its derivatives,
- basic: aniline and its derivatives, pyridine and its derivatives,
- transitional: dioxane, methoxyphenanthrene.

The carbon-insoluble fraction also contains sulfur compounds, metals and sulfate-related water[18].

3. Chemical composition of particulate matter emitted from combustion processes

There are three main types of primary particles emitted by the combustion process: soot particles, organic and inorganic particles. Soot and organic particles originate from combustible material and are formed due to incomplete combustion. Inorganic particles consist of non-combustible material and are formed in conditions of nearly complete combustion. In addition to the increased soot formation, organic compounds condense on the surfaces of primary particles or may form very small organic particles through nucleation mechanisms [11].

Below is a kind of a short overview of the selected components of PM samples from different combustion processes.

3.1. Metals

The chemical characterization of transition metals and inorganic species present on PM has been the subject of intensive studies for years. Although heavy metals account for only a small fraction of the PM 2.5, they are not only non-biodegradable when adherent to particles but they can also bioaccumulate through the food chain and contribute to the toxicity of PM_{2.5}. In earlier studies scientists reported an association between PM-bound metals and potential health effects [19]. Although heavy metals typically represent only ~10% of PM mass, they still represent environmentally important components.

Heavy metals are a major global environmental problem due to the rapid industrial growth and urbanization. The problem is driven by inadequate environmental management and lack of strict adherence to environmental protection policies.

According to the literature [20] the size distribution of trace metals has been widely linked to their sources. In coarse mode particles there were observed trace metals such as Al, Ti, Ca, Fe due to their high abundance in the crust and, thus, in mineral dust. While in the fine mode particles trace metals such as Pb, V, Ni, Zn, Se, As were often observed as they are often related to high temperature combustion emissions. Trace metals in urban and rural regions origin from mixtures of gaseous and particulate components which include of high temperature incineration and combustion plants, motor vehicle emissions, abrasion of tires or brakes, road dust, and also crustal weathering. The sources of trace metals may differ significantly, depending on the location and meteorological conditions, leading to variations in the trace metal concentrations and the composition of the aerosol.

The Directive 2000/76/EC limits the daily average air emission for total dust as well as for certain metals and their compounds, including their gaseous form. The daily average air limit for total dust within the exhaust gases is set at 10 mg m⁻³ (EU, 2010). While the average air emission limit for metals values for the sampling periods of a minimum of 30 minutes. The specified metals are cadmium and thallium (the sum of which is limited to 0.05 mg m⁻³), mercury (limited to 0.05 mg m⁻³). The average values over the sample period of a minimum 30 minutes for antimony, arsenic, lead, chromium, cobalt, copper, manganese, nickel and vanadium (the sum of them) is limited to 0.5 mg m⁻³. Limits are also set for various gaseous pollutants, including gaseous and vaporous organic substances (expressed as total organic carbon, TOC), and dioxin and furan emissions.

Sources of heavy metals include construction and demolition activities, mining and mineral processing, agricultural activities, wind-blown dust and road dust and related transportation activities. Below in Figure 1 the authors summarized the sources of heavy metals in PM.

According to the literature, different authors have assigned metals to different traffic related sources which makes it very difficult to precisely assign source attribution with trace metals alone very difficult unless detailed local information on source particle composition is available. Trace metals can be used as a source markers. Some trace elements as well as organic compounds are used

as a source markers for vehicle emissions. After the removal of lead ethyl, used as an antiknocking agent, from gasoline, the trace metals have proved to be far less useful as tracers of engine exhaust. Since then they have been the most commonly used as markers for motor vehicle exhaust particles in the atmosphere [15].

Pb
<ul style="list-style-type: none"> •The main emission source of lead in the atmosphere for many years has been the use of leaded gasoline in vehicles. Since the lead content in fuels has been regulated during the past years, industrial sources and fuel burning activities have assumed greater importance in ambient lead production.
As
<ul style="list-style-type: none"> •The main arsenic-emitting anthropogenic sources are the stationary combustion of fossil fuels, especially the coal-burning and metallurgical industry.
Cd, Ni
<ul style="list-style-type: none"> •Cadmium and nickel compounds in particulate matter, derived from coal and fuel oil combustion processes, metallurgical industry, and road transport.
Cr
<ul style="list-style-type: none"> •Compounds of chromium at the sixth valence state are widely understood to be associated with toxic and, most importantly, with carcinogenic effects of the bronchial tree. There is some evidence that the abundance of hexavalent chromium in total suspended chromium particles in urban areas is substantial. Chromium in ambient air originates mainly from metallurgical industries and oil refineries.
V
<ul style="list-style-type: none"> •The vast majority of anthropogenic vanadium emissions to the atmosphere result from combustion of crude or residual oil.
Mn
<ul style="list-style-type: none"> •The suspension of crustal particles and industrial activities are mainly responsible for the ejection of manganese in the atmosphere.
Hg
<ul style="list-style-type: none"> •Mercury and its compounds, emitted to the atmosphere through a variety of production processes. The overwhelming majority of metallic mercury and mercury compounds in the ambient air occur in the vapor phase, with the particulate fraction usually accounting for less than 5%.
Cu
<ul style="list-style-type: none"> •Emissions of atmospheric copper are mainly due to metal production and other industrial processes. However, there is mounting evidence that in urban areas, the road transport sector is a major copper emission source, through the wear of vehicles' brake linings.
Ba
<ul style="list-style-type: none"> •Used as a tracer for non-exhaust emission of PM from brake-wear. •Along with Br and Black Carbon (BC) used as a tracer for gasoline/diesel combustion.

Figure 1. Sources of the selected heavy metals in particulate matter.

3.2. Isotopes

In most cases, to identify the combusted fuel, scientists seek a source profile of elements, not just one specific element that is related to the combustion of a particular fuel. It is not just the presence of a specific element, but the chemical speciation of an element that provides information about its source. In other cases it is not the element itself, which could provide answers to source apportionment, but the isotope ratio(s) for this element [3].

Mercury in the atmosphere exists in two oxidation states, 0 and + 2, and three different operationally defined forms, Gaseous Elemental Mercury [GEM; Hg⁰], Gaseous Oxidized Mercury compounds [GOM; HgII] and Particulate/aerosol Bound Mercury [PBM; Hg(p)]. GEM is the dominant form of atmospheric mercury and generally accounts for more than 95% of total mercury in uncontaminated air. GEM and GOM can bind to aerosols or particles and the particle bound mercury (PBM) can remain in the atmosphere for several weeks before being deposited locally and regionally. In pristine rural environments, GOM and PBM are typically present in concentrations less than 10 pg/m³, but in polluted urban-industrial areas and during atmospheric mercury depletion events, their concentration levels can reach values in excess of 300 pg/m³. PBM is largely of anthropogenic origin and can account for up to 40% of total atmospheric mercury in industrialized regions. Recent measurements of PBM in several urban/industrial areas have documented that mercury can be associated with large particles (with the aerodynamic diameter larger than 2.5 µm) and in concentrations similar to those of the vapour phase mercury. GOM and PBM therefore form a significant fraction of the total atmospheric mercury emissions, particularly during coal combustion and municipal waste incineration [21-23].

A major challenge in source apportionment studies of Hg remains in the fact that it is difficult to identify and quantify different sources once mercury is dispersed and intermixed in the environment. The discovery of mass dependent fractionation (MDF) and mass independent fractionation (MIF) of mercury isotopes have paved the way to a new method for tracing Hg pollution and investigating mercury behaviour in the environment. Mercury has seven stable isotopes (¹⁹⁶Hg, ¹⁹⁸Hg, ¹⁹⁹Hg, ²⁰⁰Hg, ²⁰¹Hg, ²⁰²Hg and ²⁰⁴Hg).

To the best knowledge of the authors, only one study has explored the mercury isotopic composition of PBM which can form an important component of atmospheric Hg deposition in urban environments[24].

Radioactive carbon (¹⁴C) is an ideal tracer to distinguish the fraction of fossil fuels from contemporary components in the carbonaceous matter. Since the contemporary sources mainly consist of biomass burning, biogenic emissions (secondary organic carbon from the biological volatile organic compounds), and soil dust, their ¹⁴C contents are different. The contributions of the contemporary sources to the carbonaceous matter may be estimated based on the mass balance of ¹⁴C. Additionally, the fossil fuels have their identifiable stable carbon composition (δ¹³C). According to the mass balance of ¹³C, contributions of coal burning and vehicle exhaust to the carbonaceous matter may be further estimated on the basis of the assumption that the fossil fuel emissions mainly include coal burning and vehicle exhaust[25].

3.3. Sugars

Biomass burning is a significant source of aerosol particles emission to the atmosphere, and its contribution to the carbonaceous aerosol in urban sites has been recognised as a substantial. Chemical analysis of the combustion particles of wood, peat and fossilized cellulose-containing coal, revealed that anhydro-monosaccharides represent a main fraction of water soluble organics with levoglucosan (1,6-anhydro-β-D-glucopyranose) being the most abundant species[26]. Levoglucosan-like species (levoglucosan, mannosan, galactosan) are anhydro-saccharides formed in the pyrolysis of cellulose and common organic molecular constituents of biomass burning emissions. Many studies worldwide, especially those conducted at Technical University of Wien, have used

levoglucosan (dominant anhydro-saccharide emitted) as a distinctive biomass burning chemical signature [9] [27].

Levoglucosan (1,6-anhydro- β -D-glucopyranose) is considered a highly specific tracer for biomass burning aerosols, because it derives from the pyrolysis of cellulose and hemicellulose at high temperature (higher than 300°C). It is a perfect molecular marker because it is relatively stable in the atmosphere and is emitted in large amounts. Levoglucosan is concentrated mostly in fine fraction of PM. Its specificity, photochemical stability and significant emissions in woodsmoke allow its concentration to be reliably assessed. Because of its stability and concentration in the fine fraction, levoglucosan concentrations may be affected by regional sources. Concentrations of levoglucosan have been measured in a variety of areas across Europe, but studies differ widely in the season of measurements, the type of location e.g. remote, rural or urban, PM size fraction and sampling method.

Annual average concentrations of levoglucosan reported across Europe varied significantly from a few to hundreds of ng/m³. Clear seasonal variation has been reported with higher concentrations found in the cold season. The variation of levoglucosan levels in these different studies may be due to differences in wood burning, but methodological differences may contribute as well [28].

Levoglucosan is specific to the combustion of cellulose containing materials and no other sources are currently known to exist. Major known sources of levoglucosan are fuel wood combustion in the winter season and agricultural, garden waste burning and forest fires, particularly in Mediterranean countries, especially in the summer [29]. Due to its source-specific emission and atmospheric stability, levoglucosan is an important molecular source tracer for fine particle emissions from biomass combustion. While emission factors of the levoglucosan isomers, mannosan, and galactosan, are typically lower than those of levoglucosan, these anhydro-sugars can be utilized as biomass combustion tracers as well.

Mannosan, a pyrolysis product from hemicelluloses, is the second most abundant anhydro-sugar in the wood smoke samples.

Considering the ratio of levoglucosan to mannosan, the difference between hardwood (beech, oak) and softwood (spruce, larch, briquettes) types is well visible. Schmidl et al. [9] found that hardwoods give high ratios, around 14-15, while softwoods give low ratios, 3.6-3.9. Softwood briquettes exhibit a ratio of 2.5 – somewhat lower than the corresponding ratio for log wood. Therefore the proportion of soft- and hardwoods can be estimated from the levoglucosan to mannosan ratios in ambient PM by applying the following equation:

$$\% \text{spruce} = \frac{14.8 - R_{\text{leve/man}}}{0.112},$$

where $R_{\text{leve/man}}$ is the ratio of levoglucosan to mannosan concentration in ambient air; 0.112 the slope of the linear correlation between levoglucosan/mannosan ratios and contribution of spruce smoke to ambient wood smoke levels [9].

3.4. Oxygenated Polycyclic Aromatic Hydrocarbons

Among the wide range of organic compounds that are associated with PM, the rather non-polar fraction has attracted the greatest deal of attention. Particularly, the identification and quantification of polycyclic aromatic hydrocarbons (PAHs) has been investigated intensively. This is mainly because of the well-known carcinogenic and mutagenic properties of this group of compounds. The occurrence and the analytical techniques used for determination of PAHs have been widely reported and therefore they will not be subject of this paper.

One component class that deserves major attention consists of the oxygenated polycyclic aromatic hydrocarbons (PAHs). Those compounds are considered to be among the key compounds in the toxicity of PM. In agreement with Lundstedt et al. (2007), oxygenated PAHs are PAHs oxidation products that can be divided into two sub-groups: oxy-PAHs and hydroxylated PAHs. Oxy-PAHs contain one or more carbonyl oxygen(s) attached to the aromatic ring structure and consist of ketones and quinones. While hydroxylated PAHs are defined as PAHs on which one or more hydroxyl groups are attached. Strong indications of the toxicological importance of oxygenated PAHs have

resulted in a growing interest in the chemical analysis, occurrence, fate and behaviour of these micropollutants on PM.

The PAHs derivatives formed through atmospheric reactions with oxidative species such as ozone, hydroxyl and nitrate radicals as well as UV induced photoreactions. These PAHs oxidation products are typically found in the intermediate polarity PM fractions and include a wide range of compounds that can be classified as nitro-PAHs and oxygenated PAHs.

Figure 2 summarizes the fate and behaviour of oxygenated PAHs in the environment. There are limited experimental data about physical and chemical properties of oxygenated PAHs. The fundamental research on these properties needs to be conducted in order to furnish a better understanding of the environmental and toxicological behaviour of oxygenated PAHs.

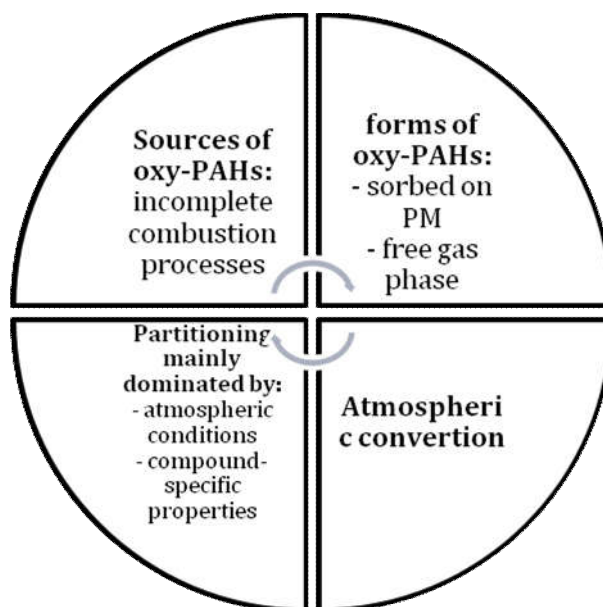


Figure 2. The atmospheric fate and behaviour of oxygenated PAHs.

Oxygenated PAHs are typically characterized by higher molecular weights and lower vapour pressures compared to their parent PAHs (Figure 3).

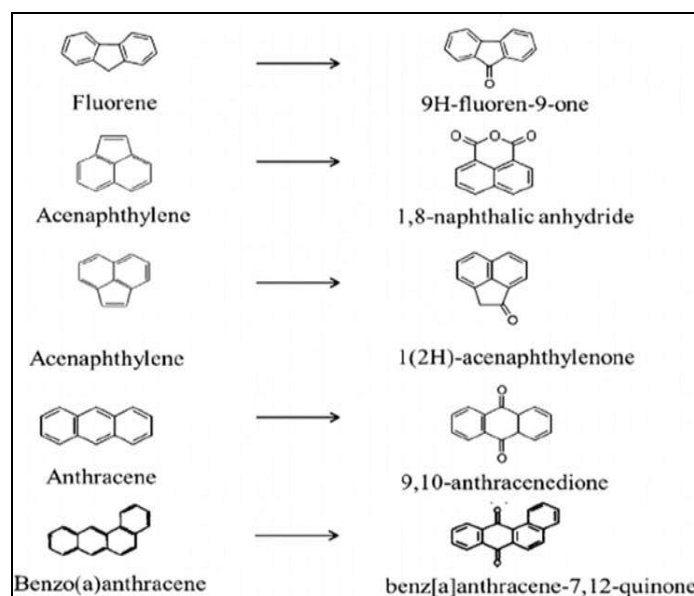


Figure 3. Oxy-PAHs and their corresponding parent PAHs[30].

Vapour pressure is a crucial parameter affecting the partitioning of organic compounds between the free gas phase and the particulate phase in the atmosphere and since the vapour pressure of oxygenated PAHs is well below 10 Pa at ambient conditions, it is clear that oxygenated PAHs have a higher tendency to sorb onto PM than their parent PAH compounds[31].

In contrast to PAHs which are emitted directly from combustion processes, the sources of oxygenated PAHs emission to the atmosphere can be both by tropospheric conversion of PAHs and by direct introduction.

Oxygenated PAHs can be formed out of PAHs via photochemical reactions and reactions with hydroxyl radicals, nitrate radicals and ozone. Given the partitioning of PAHs between the gas phase and PM, transformation processes can take place in both phases. Reactions involving hydroxyl radicals (during day) and nitrate radicals (during night) are considered to play a major role in gas phase reactions whereas ozone and photolysis are expected to play only a secondary role. Particle associated PAHs containing more than five rings are less susceptible to reaction with gaseous reactive radicals.

Nevertheless, they can also undergo a wide variety of transformation processes, but often with slower kinetics than in the gas phase.

Direct emission of both gaseous and PM associated oxygenated PAHs proceeds through incomplete combustion processes of a wide variety of materials. Major sources are the combustion of domestic waste and biomass and the open burning as well as smoldering of building debris. They are also compounds of diesel PM and are emitted during gasoline combustion, production of charcoal and coal burning.

3.5. Hopanes, steranes

Vehicle exhaust emissions are one of the most important anthropogenic sources of air pollutants. Exhaust emissions depend on many factors, e.g., type of fuel, its quality, type of engine, after-treatment technologies, engine operating conditions, and engine wear and maintenance. Semivolatile organic compounds (SVOCs) in vehicle exhaust are found in both solid and vapour forms and, besides polycyclic aromatic hydrocarbons (PAHs), include nitro-PAHs (NPAHs), hopanes, steranes, and numerous other compound classes[32].

Hopanes and steranes are common constituents of crude oil and are also present in lubricating oil used by both gasoline- and diesel-powered motor vehicles, as well as they are also found in diesel fuel [33,34]. As those compounds are resistant to chemical, photochemical and microbial degradation,

hopanes and steranes have been widely used as a biological marker or as a tracers of vehicle exhaust in the atmosphere (given their specificity to lubricating oils used in diesel and gasoline engines. Hopanes can also be used as organic markers for fossil fuel combustion where they are used for sorting of coal according to its age [35]. One observed that hopanes (not steranes) are also present in smoke of coal combustion. A few studies indicated that hopane and sterane emission rates were not affected by alternative fuels such as biodiesel.

In comparison to other PM components (like OC, EC, PAHs) hopanes and steranes have relatively low overall emission factors. One reported, that according to the tunnel study which apportioned emission factors between light-duty vehicles and heavy-duty vehicles hopane and sterane emission factors for heavy duty vehicles were approximately 8 -14 times greater than light duty vehicles for ultrafine PM (dynamic diameter $dp < 0.18 \mu\text{m}$) and 10-20 times greater for accumulation PM ($2.5 > dp > 0.18 \mu\text{m}$) [36].

It was observed that disproportion between the concentrations of R- and S- isomer of 17α (H), 21β (H)-homohopane points to different emission sources. The similar concentrations of R and S isomers indicate traffic emissions, while much higher concentrations of R isomer than S isomer indicate coal combustion. One observed that when the ratio of R- and S-homohopane, $S/(S+R)$ ranged between 0.012 and 0.074, it suggested that the main emission source of hopanes was combustion of lignite or brown coal [35].

4. Conclusions

It is very important for the environment, to understand the principles and quantitative contributions of the combustion processes to the PM emissions. A significant amount of research has been carried out on characterization and analysis of exhaust emissions. Exhaust emissions from traffic are constantly changing as abatement technologies develop. An improved understanding of the chemical characteristics of PM of traffic origin and identification of their specific sources are needed for the development of the air pollution control strategies.

Nowadays non-exhaust emissions are becoming more important. Further research is anticipated in this field in the coming years due to the rapid growth of electric vehicles.

The characteristics of the sources of origin of oxy-PAHs in particulate phase will facilitate the understanding of the behaviour of oxy-PAHs in the environment. While chemical characterization of PM emitted from combustion processes including the analysis of metals and metalloids will allow scientists to create a source profile of pollutants. Isotopic analysis as an innovative element of analytical chemistry, can facilitate the future identification of the sources of air pollution.

In recent years the development of a health-oriented air quality management strategy has received considerable attention in order to soothe human health risks. However, most of the air quality standards and health-risk assessment studies are still based on the mass concentration of PM_{2.5}. More detailed risk assessment studies dealing with the detailed chemical speciation of specific source-related PM_{2.5} are needed.

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