Organic Species Emitted as a Part of Combustion Residue: Fate and Transformation in the Ambient Air

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ABSTRACT

Organic species emitted as a part of combustion residue are one of the major components of both gaseous and particulate emission. These species gets diluted and transformed when they come in contact with the atmospheric gases. The gas to particulate conversion of SVOC (semi volatile organic compound) leads to the formation of SOA (secondary organic aerosol). Gas to particle conversion is very sensitive to the level of dilution. Combustion generated particulates are formed as a result of a complex process. The precise mechanism of SOA formation is still not completely understood but it is largely attributed to oxidation of reactive organic gases (ROGs) and gas to particle phase conversion. Polycyclic aromatic hydrocarbons (PAHs) present in the combustion products may also get transformed upon dilution and oxidation when emitted in the ambient atmosphere. PAHs and their derivatives are formed by the incomplete combustion of organic materials arising from combustion and due to anthropogenic emissions. The PAH concentration varies significantly in various rural and urban environments and their concentration are mainly influenced by the level of vehicular and domestic emissions. Diagnostic ratio (DR) approaches allow either individual PAHs or their combination to be used for identifying their origin sources. This paper discusses the fate and transformation of SOA and Polycyclic aromatic hydrocarbons (PAHs) largely emitted from combustion sources. The effect of temperature and relative humidity on the formation of SOA and a brief discussion on its measurement and analysis has also been described in this study. Finally, a brief discussion on various health effects attributed to combustion generated species has been provided.

1. Introduction

Poor air quality attracts a high level of interest among the scientific community and engages public in various forums due to the known relationship between exposure to many air pollutants and increased adverse health effects on the human health (Yang and Omaye, 2009; Ruckerl et al., 2011). In addition, air pollution can seriously deteriorate visibility (Hyslop, 2009) may damage buildings materials and cultural heritage (Watt et al., 2009) and has direct and indirect effects upon climate (Ramanathan and Feng, 2009; Jaidevi et al., 2011). While air pollution remains a major problem for developing countries (Fenger, 2009; Liaquat et al., 2009) because of the rapid growth of population, energy demand and economic growth, developed countries have largely experienced significant decline in the concentrations of many air pollutants over the past decade (Fenger, 2009; Liaquat et al., 2009). In early nineteenth century, fossil fuels have dominated transportation sector since the invention of internal combustion (IC) engines. In order to effectively control environmental pollution and alleviate its harmful effects, exhaust characterization at the engine outlet is essential (Eastwood, 2008).

Exposure to particulates emitted from vehicular tail pipes lead to adverse health effects on our health which largely depends upon the physico chemical composition of these particles. PM properties determine their true residence time and availability as sorption sites and their deposition inside the human respiratory system (Schroedar et al., 1999; Krahl et al., 2008, 2003; Agarwal et al., 2013, 2011). Complex processes in the combustion chamber such as air–fuel mixing, combustion chamber geometry, fuel droplet spray, and temperature and pressure conditions of the cylinder charge during combustion dictate the type and amount of PM formation that is emitted in the tail pipe (Flynn et al., 1999; Dhar and Agarwal, 2013). Formation of particulates in a diesel engine is very sensitive to actual air–fuel ratio present in the premixed reaction zones of the combustion chamber where soot precursors are initially generated (Flynn et al., 1999).

Diesel engines are among the most efficient power sources, which emit comparatively lower amounts of CO and HC emissions as compared to the gasoline engines but higher amounts of oxides of nitrogen (NO_x) and particulate matter (Agarwal et al., 2015). NO_x and PM are both related with deleterious effects on the human health.

2. Chemical characterization of particulate matter

2.1. Chemical composition of particulate matter

Heterogeneous combustion takes place inside the diesel engine. Fuel is injected into the combustion chamber towards the end of the compression stroke in a conventional CI engines. Modern diesel engines are equipped with common rail direct injection (CRDI) system, and split injection capabilities, i.e. fuel can be injected in pilot injection, main injection and post injection in the same engine cycle. When fuel is injected into the combustion chamber at a very high injection pressure, it breaks

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into large number of small droplets under the influence of high combustion chamber pressure, prevailing at the end of compression stroke. Resistance to high pressure fuel droplets are generated by compressed air in the combustion chamber, which produce further fragmentation of small droplets into finer droplets and results in a better combustion scenario.

The diesel particulate matter (DPM) is comprised of elemental carbon, organic carbon, nitrates, sulfates and metals (in trace quantity) (Fig. 1). DPM can act as an excellent carrier for adsorbed organic and inorganic compounds due to its large surface area. Mass of emitted particles per mile from diesel engines are nearly 10 times higher than that of a conventional gasoline engines, and 30–70 times more than the engines equipped with catalytic converters (Godlee, 1993).

A major portion of DPM has a size smaller than 1 μm. The residence time of its constituents in the atmosphere may change from a few hours to several days. These particles can travel long distances and, are also capable of penetrating to our deeper parts of our lungs and in turn can cause adverse health effects as ultrafine particles can also enter in the blood stream and get translocated to different vital organs (Agarwal et al., 2015; Gupta et al., 2010).

2.2. Occurrence of Elemental and organic carbon (EC/OC)

Elemental carbon and organic carbon are the two main constituents of the combustion exhaust particulates. A large number of studies have explored the EC and OC content of diesel particulates. As a consequence of heterogeneous combustion with the CI engines, unburned and partially burnt hydrocarbons are emitted. Under high temperatures and pressures present inside the combustion chamber, a fraction of hydrocarbons, which are present in a locally fuel rich, undergoes pyrolysis and lead to the formation of nuclei mode particles (Fig. 2). Most of the hydrogen atoms get stripped off the hydrocarbon chains and only carbon atoms remain. As a result of this, carbon core formation takes place, which is also called as 'soot'. Carbon undergoes cyclization, and sheet like structure formation and eventually nano–tube like structures called spherules are formed (Abbass et al., 1991).

Volatile organic materials usually condense over the solid and dry soot and these particles further grow. This condensed organic material also known as the soluble organic fraction is extremely harmful for humans. This condensed organic matter contains hundreds of organic compounds formed as a result of complex organic species formation pathways during fuel pyrolysis inside combustion chamber. Some of the organic compounds are known carcinogens such as polyaromatic hydrocarbons (PAHs), Benzene–Toluene–Ethyl–benzene–Xylene (BTEX).

2.3. Unregulated emissions

Regulated gases (CO, THC and NOx) and particulate matter (PM) are currently covered by legislations for their control. Vehicles/ engines also emit large number of other emissions, most of which are in very small quantities except CO_2 and moisture, which are classified as unregulated emissions. In some emission legislations, CO_2 is now included as regulated species. Unregulated emissions are important from health point of view. Ravindra et al. (2008) signaled in their research that there should be emission regulations for carcinogenic compounds like PAHs, carbonyl compounds and BTEX as these are toxic species emitted by diesel engines.

2.3.1. Carbonyl compounds

A large number of different harmful compounds are emitted by diesel engines and many compounds are still unknown. The term carbonyl signifies to the carbonyl functional group, which is a divalent group comprising of a carbon atom double–bonded to oxygen. Carbonyls have significant occurrence in the engine exhaust. Various studies have assessed carbonyl emissions by using its derivatives with 2, 4–di–nitro–phenyl–hydrazine (DNPH) (McDonald et al., 2004; Schauer et al., 1999; Schauer et al., 2002; Grosjean et al., 2001; Kristensson et al., 2004).

Carbonyl emissions result in the formation of secondary organic aerosols (SOA) by forming oligomers (Loeffler et al., 2006). Contribution of carbonyls in diesel particles also augments their physiological response (Madden et al., 2003). Pang et al. (2006) examined the characteristics of carbonyl emissions from a diesel engine fuelled with biodiesel–ethanol–diesel blend. They found that acetaldehyde was the carbonyl compound emitted in the highest concentration, followed by formaldehyde, acetone, propionaldehyde and benzaldehyde, respectively. They reported 1–12% higher total carbonyl emissions with biodiesel–ethanol–diesel blend depending upon the engine operating condition. They also reported that carbonyl emissions increased with increasing engine speed while minimum carbonyl emissions were found at 50% engine load, when the engine was operated at a constant speed (Ho et al., 2012).
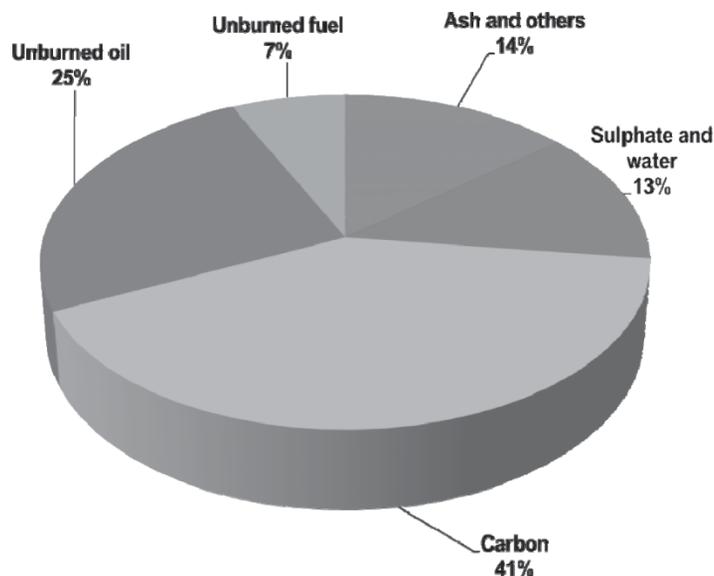

Figure 1: Composition of typical diesel particulate (Adapted from Kittelson, 1998)
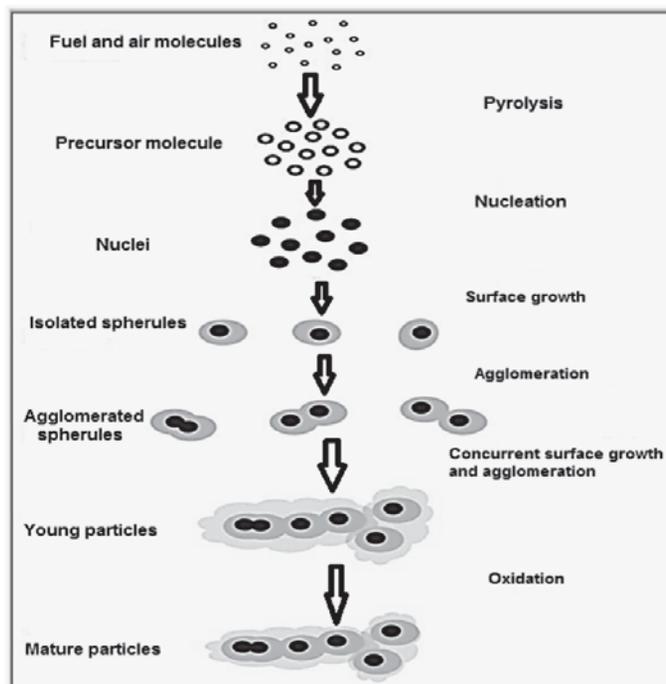

Figure 2: Schematic view of soot formation adopted from particulate emissions from vehicles by (Adapted from Eastwood, 2008)

Ho et al. (2012) measured and quantified 15 different carbonyl species and formaldehyde was the most dominant compound, followed by acetaldehyde and acetone. They observed that formaldehyde was 54.8–60.8% of the total carbonyl compounds present in the exhaust. They took samples at various locations in the city of Hong Kong and found that the formaldehyde concentration was quite high as compared with the theoretical value predicted in summer, which suggests significant effect of photochemical reactions in formaldehyde production in the ambient atmosphere.

2.3.2. Benzene, toluene, ethyl–benzene and xylene (BTEX)

Petroleum products such as gasoline include these compounds (BTEX), which have harmful effects on humans. Cheung et al. (2009) reported levels of BTEX emissions from a diesel engine fuelled with mineral diesel, biodiesel and biodiesel blends with methanol (5%, 10%, and 15%) at a constant engine speed of 1800 rpm and compared for five

different loads. Higher oxygen content in the biodiesel fuel leads to oxidation of BTEX. They reported that higher engine load resulted in lower BTEX emission in the engine exhaust.

Di et al. (2009) and Takada et al. (2003) also observed lower BTEX emissions at higher engine loads. Ballesteros et al. (2008) used biodiesel and reported relatively lower aromatic emissions. Machado and Arbilla (2008) obtained a strong correlation between carbonyl emissions and biodiesel content ($R^2 > 0.96$). They reported that esters in biodiesel may be a main source of these carbonyl emissions. Liu et al. (2009) and Cheung et al. (2009) signified that carbonyl emissions increase with increasing biodiesel content at lower engine load however; they get reduced at higher engine loads. Xue et al. (2011) concluded that biodiesel reduces the emission of aromatic and poly–aromatic compounds. They also recommended that carbonyl emissions increase in general with biodiesel content because biodiesel provides extra inherent oxygen present within the fuel molecules.

2.3.3. Polycyclic aromatic hydrocarbons (PAHs)

PAHs are well known carcinogens and are produced due to both incomplete combustion of fuel. Ravindra et al. (2008) organized a database to recognize and characterize the PAH emissions in their study. They also reported the factors affecting PAH emissions. Most of the possible human carcinogenic PAHs were found adsorbed on to the PM surface. There are no rigorous regulations for PAH emissions but these pollutants should get high priority due to their adverse impact on the human health. Fig. 3 shows the USEPA priority listed PAHs. Some of compounds shown in Fig. 3 are conceived as 'probable human carcinogen' (B2), while some are not listed as 'human carcinogens' (D) (Ravindra et al., 2008). Singh et al. (2015) measured the total average mass concentration of 16 major PAHs in a study carried out in Kanpur during fog time collected PM_1 and it was found to be 616.31 ± 30.31 ng/m³. Similarly, other studies carried out in the ambient air of different places around the world for different particle size are shown in Table 1.

Table 1. A summary of total PAHs concentration (ng/m³) in various cities of the world (Adapted from Singh et al., 2015)

Study area	Particle size	No. of PAHs	"PAH (ng/m³)
Chennai, India	$PM_{2.5}$	11	517.1
Coimbatore, India	PM_{10}	13	90.4
Agra, India	PM_{10}	18	97.9
Delhi, India	TSP	12	669.9
Kanpur, India	PM_1	16	616.31
Seoul, South Korea	TSP	15	89.3
Tehran, Iran	PM_{10}	16	44.2
Mexico City, Mexico	$PM_{2.5}$	11	310
Shenzhen, South China	TSP	16	128
Taiyuan, China	TSP	8	1,504.7

The toxicity of these PAH compounds are highly dependent on their molecular structure. Two isomers of PAHs with different structures show different toxicity. Therefore, EPA has classified these PAH compounds into different categories. Lea–Langton et al. (2008) collected particulate samples for diesel, biodiesel and cooking oil for comparison and analysis of particulate bound PAH emissions from a heavy duty DI diesel engine. Most of the particulate bound PAHs were lower in both the biofuels compared to mineral diesel, especially at low load conditions and most of the larger PAHs such as benzo(a)anthracene, chrysene, benzo(b)fluoranthene and benzo(k)fluoranthene were oxidized by diesel oxidation catalyst

(DOC). They also conveyed that fluoranthene was absent in mineral diesel but was present in particulates, which was an indication of pyrolytic formation of fluoranthene in engine combustion chamber.

Zielinska (2005) assessed physical and chemical transformations of primary diesel emissions. They found that transformation of primary diesel emissions in the atmosphere is very crucial from the human health perspective. Primary diesel exhaust reacts primarily with OH radicals, ozone, NOx radicals and sunlight present in the ambient air. Monocyclic aromatics of primary diesel exhaust reacts with OH radicals and produce various aromatic compounds such as phenols, glyoxal, quinones, nitro–PAHs, and aromatic aldehydes.

Recently, it is reported that PAHs presents in the diesel particulates are one of the key factor, which adversely affect human health. PAHs include various PAHs, which reveal different toxic properties. EPA has listed 16 PAHs as carcinogenic, probable carcinogenic and possible carcinogenic and the molecular structure of these are shown in Fig. 3.
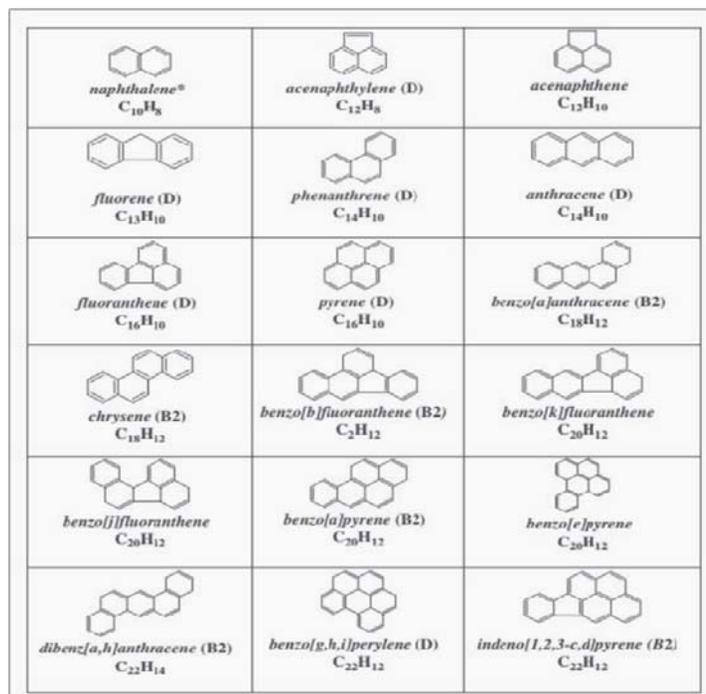
Figure 3. Priority listed PAHs.*Not included in priority list; D (not listed as to human carcinogenicity); B2 (probable human carcinogen) (Adapted from Ravindra et al., 2008)

Researchers (Karavalakis et al., 2009; Pan et al., 2000) have presented detail speciation of PAHs adsorbed on the diesel particulates. Each PAH has a different toxic potential for carcinogenic effects hence speciation of PAHs is a very important (Nisbet and LaGoy, 1992). There are some studies, which inform about the toxic potentials of individual PAH species. A summary of total PAHs concentration (ng/m³) in ambient air of various cities in the world is shown in Table.1.

Singh et al. (2015) reported that, diesel engine is the main source of PAHs by analyzing the fog time collected PM_1 by diagnostic ratios, shown in Table 2. Figure 4 shows the speciation of major PAHs concentration

Table 2. Diagnostic ratios (DR) of PAHs used as source indicator and comparison of diagnostic ratios of fog time collected submicron particles in Kanpur (Adopted from Singh et al., 2015)

| Diagnostic ratio (DR)	Value	DR (sources)
Indeno[1,2,3cd]pyrene/(Indeno[1,2,3–cd) pyrene +benzo[ghi]perylene	0.58	0.56 (coal) and 0.35–0.70 (diesel)
Indeno[1,2,3 cd)pyrene/benzo[ghi]perylene	1.37	<"1 (diesel)
Fluoranthene/(fluoranthene+pyrene)	0.73	>0.5 (diesel)
Benzo[b]fluoranthene/benzo[k]fluoranthene	0.62	>0.5 (diesel)
B[a]P/Benzo[ghi]perylene	1.17	0.5–0.6 (traffic emission)>1.25 (brown coal)[a]
B[a]P/(B[a]P+chrysene)	0.39	<"0.5 (diesel)
Pyrene/B[a]P	2.22	<"1 (petrol engine)<"10 (diesel engine)
Fluorene/(fluorene+pyrene)	0.55	>0.5 (diesel)
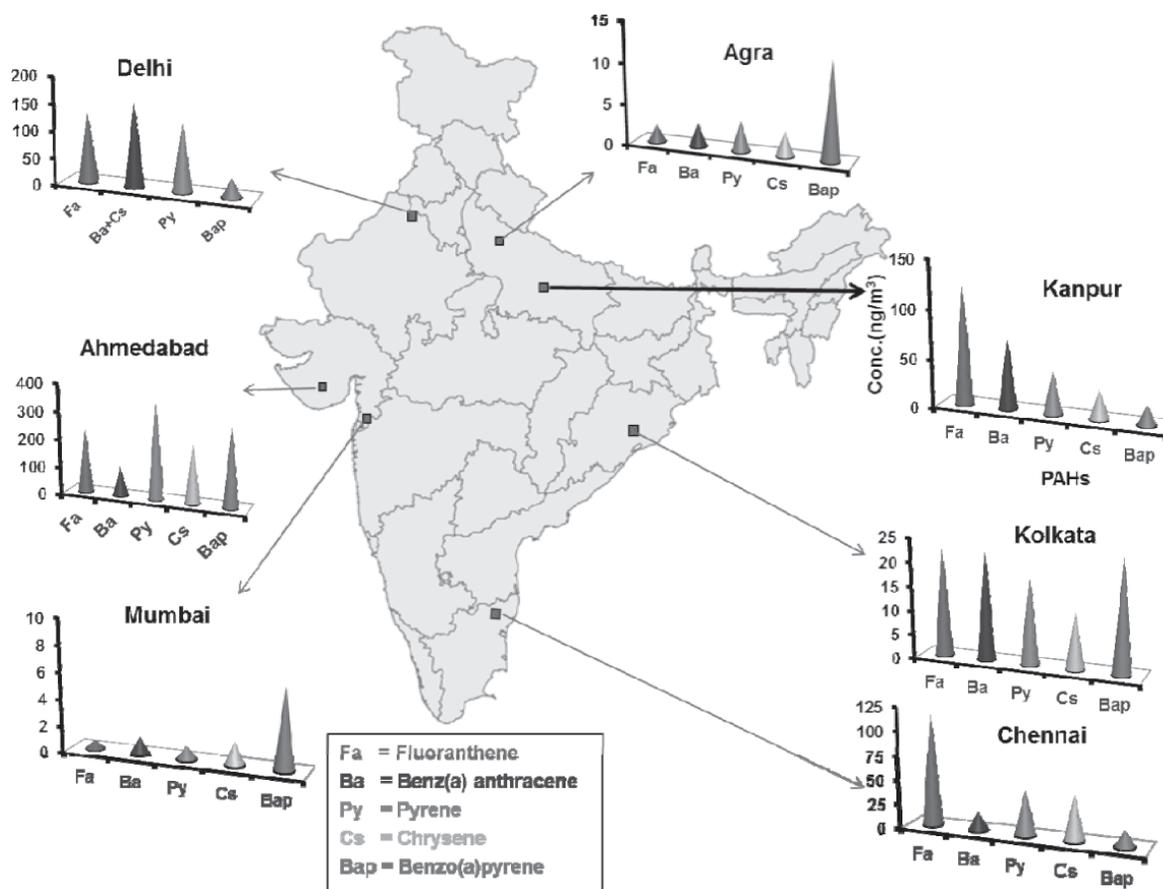
Figure 4: Speciation of major PAHs concentration (ng/m³) of high molecular weight PAHs and Benzo[a]pyrene in some major cities of India (Adapted from Singh et al., 2015)

(ng/m³) of high molecular weight PAHs and benzo[a]pyrene in some major cities of India (Singh et al., 2015). Polycyclic aromatic hydrocarbons (PAHs) are one of the most toxic and harmful class of chemical species present in the engine exhausts (Gupta et al., 2010).

Diesel emission is comprised of a complex mixture of various organic compounds (OC) or soluble organic fraction (SOF), nitrates, sulfate, metals, and irritants (such as acrolein, ammonia, PAHs) which are usually adsorbed over elemental carbon (EC) core. Excessive operation of diesel engines given their fuel economy, durability and power advantage has given rise to exponentially higher levels of diesel exhaust emissions. Diesel emissions are mainly categorized as regulated emissions (nitrogen oxides, unburnt hydrocarbons, carbon monoxide and particulates) and unregulated emissions (aldehydes, benzene, toluene, xylene (BTX), polycyclic aromatic hydrocarbons (PAHs), etc.) (Dusek and Amann, 2000).

Current emission standards look merely at the mass concentration of tail pipe exhaust. However, recent studies have associated the deleterious human health effects to the overwhelmingly large number of tiny diesel exhaust particles (Diaz et al., 2012). Recent efforts of reducing emissions have focused on advancements in combustion, engine technology, high pressure fuel injection jets, and use of enhanced after–treatment and PM control technologies (Khair and Majewski, 2006). Even though mass emissions have lowered significantly from the modern diesel engines, particle number emissions still continue to rise up (Gupta and Agarwal, 2010).

Bergmann et al. (2009) showed that diesel particulate filters (DPF) significantly lower the PM mass emitted from the diesel engine. However, more number of nuclei mode particles are emitted downstream of DPF and it also lead to more number of particles formed due to gas to particle emission with abundance of sulphate particles (Bergmann et al., 2009).

Particles formation in the exhaust tail pipe is a fairly complicated process. VOC get condensed over nuclei seed particles, get diluted and undergo oxidation upon being emitted into the atmosphere. Gas to particle conversion process is aided by the various oxidizing agents present in the ambient air (Kaul et al., 2011). Upon exiting the tail–pipe, emissions undergo cooling and oxidation and the secondary emissions like secondary organic aerosol (SOA) are formed. The ambient temperature, the amount and time of dilution dictates the resultant aerosol properties (Robinson et al., 2007).

About 90% of the PM mass for the diesel exhaust is present as two submicron modes: a nuclei–mode (7.5–56 nm); and accumulation mode (56–1000 nm) (Johnson et al., 1992). Primary carbon spheres with adsorbed organics along with sulphate form accumulation mode (Baumgard and Johnson, 1992). The nuclei mode on the other hand is dominated by the elemental carbon (EC). Several studies have shown that higher amounts of fuel sulfur results in higher number of nuclei–mode particles (Baumgard and Johnson, 1992; Opris et al., 1993). In order to examine the contribution of lubricating oil and diesel to resulting PM emission, researchers have conducted various parametric investigations (Abbass et al., 1991). About one–fourth of the unburned diesel and three–fourths of the lubricating has been shown to contribute towards the soluble organic fraction (Kittelson, 1998). A very tiny portion of SOF mass also results from pyrolysis and incomplete combustion of diesel (Figure 5).

Ultrafine particulates emitted from a diesel engine have a very high number concentration, a tiny mass concentration, and a large surface area. Due to this large surface area, they provide sorption sites for other contaminants (Cass et al., 2000). By use of mass spectrometry one recent study showed strong evidence that unburnt lubricating oil was the main source for the organic components of nanoparticles (Tobias et al., 2001). Another study showed that about 1% of the SOF was monocarboxylic acids, and about 90% of them were either unbranched, or cyclic alkanes (Rogge et al., 1993). The rest of the particles were refractory materials like oxides of the metals.
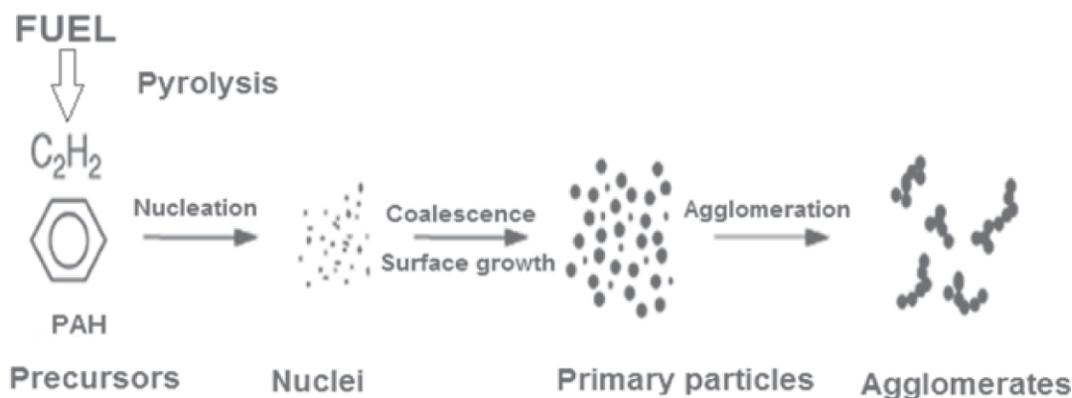
Figure 5: Schematic diagram of particulate formation during a typical combustion process (Adapted from Eastwood, 2008)

Diesel engine emissions also consists of PAHs and PAH–derivatives and they are distributed both in the gas and particle phase as they are formed at high temperature (Bildeman, 1988; Kittelson, 1985). They can get transformed to nitro–PAHs upon reaction of parent hydrocarbons with ambient NOx. Unburned PAHs present in the fuel, the electrophilic nitration of PAHs in the engine, crankcase oils, are the major source of emitted PAHs. A wide variety of both gas– and particle– phase PAHs are present in the diesel exhaust (National Research Council, 1999; Jensen and Hites, 1983; Barbella, 1988).

One study reported presence of over 100 oxy–PAH polar fractions of a diesel PM extract (Schuetzle and Frazier, 1986), and it contained species like hydroxyl, ketone, acid anhydride, and nitro –PAH derivatives. It has been reported that majority of the nitro–PAH are formed during the expansion/exhaust stroke. PAH emissions levels from heavy–duty diesel engine vehicles are reported to be much higher as compared to those emanating from light–duty gasoline cars (Honda, 1984). The diesel fuel structures and the operational engine parameters largely affect both the chemical composition as well as the toxicity of the diesel emissions (Westerholm and Li, 1994). Hence, by reducing the fuel PAH contents we can significantly lower the toxicity of the engine exhaust.

3. Secondary organic aerosol

Organic compounds contribute as a dominant portion of the ambient aerosols (Seinfeld and Pandis, 2012). Present analytical methods have facilitated us to quantitatively evaluate these organic fractions. The oxidation of Volatile Organic Carbon (VOC) results in the formation of Secondary Organic Aerosol (SOA). The composition and formation mechanism for SOA needs to be carefully studied to effectively control it.

3.1. SOA formation

Oxidation of the reactive organic gases (ROG) results in the formation of SOA. Natural as well as anthropogenic sources such as solvents, vegetation and ocean emissions, combustion of wood, biomass, and fossil fuels etc. are accountable for ROG formation (Seinfeld and Pandis, 2012; Jacobson et al., 2000). The most common ROG found in the atmosphere are alkanes, alkenes, aromatics and phenols. Semi–volatile organic carbon (SVOC) is formed via oxidation of the precursor ROGs.

The species having their saturation vapor pressure below a certain pressure are known as semi–volatile (Turpin et al., 2000). The rate of oxidation of precursor ROGs should be high in order for SOA formation to take place. Next comes partitioning of the SVOCs into the aerosol phase. There should be sufficient amount of SVOC having low saturation vapor pressure. Thus, SOA formation intrinsically depends upon reactivity or volatility (Grosjean and Seinfeld, 1989). Figure 6 shows a schematic view of SOA formation in the atmosphere.
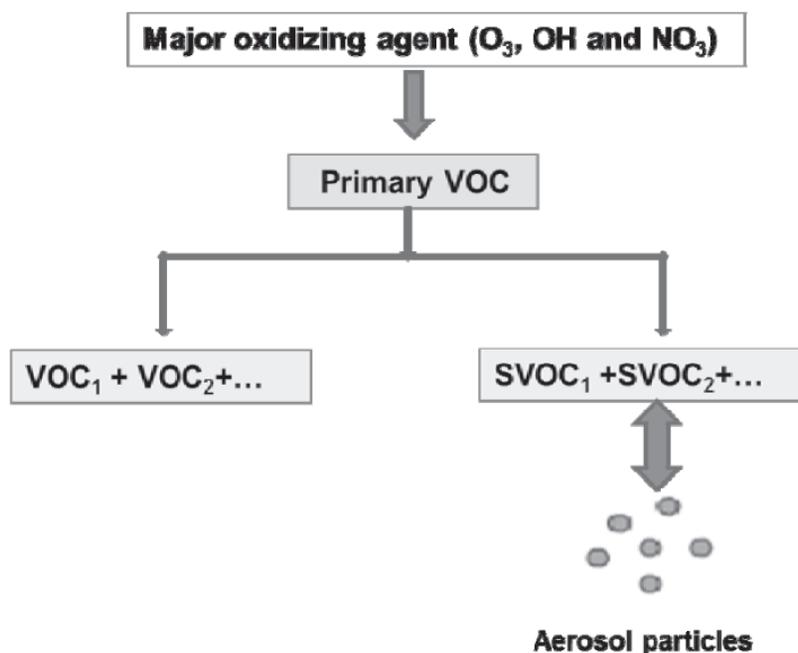

Figure 6: Schematic overview of SOA formation (Adapted from Dusek and Amann, 2000)

Present analytical methods can recognize only a few of the reaction products obtained from the oxidization of the precursor ROGs. This is the major reason identified for the lack of complete understanding of SOA. GC/MS methods can only identify a few of the organic compounds in the aerosol; hence the pathways predicted from this method do not give the total mass of the SOA formed. FTIR microscopy also does not give the information on individual species (Holes et al., 1997; Blando et al., 1998).

Therefore, the information of the various pathways of oxidization of the precursor VOCs and properties of the aerosol formed leftover is still incomplete. The oxidation of trimethylbenzene can give an indication of some of the difficulties in identifying the oxidation pathways. The oxidation of trimethylbenzene by OH radical can occur either by the addition of OH radical to the ring or by the abstraction of a hydrogen atom (Seinfeld and Pandis, 1998).
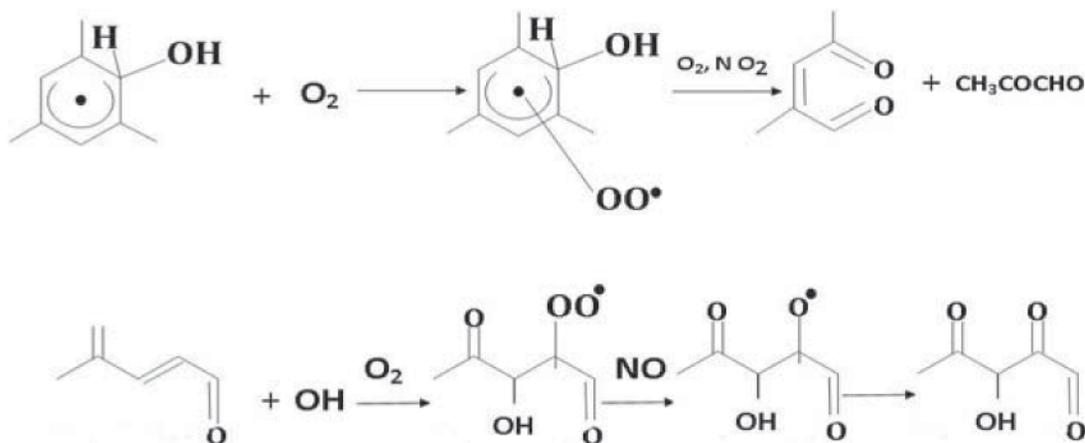

Schematic view of abstraction and addition pathways, adopted from Holes et al. (1997).

Compounds like aromatic aldehydes and aromatic nitrates are the end products of the hydrogen abstraction pathway. There is another pathway that can lead to the formation of multifunctional aromatics with nitrate and hydroxyl groups, or unsaturated dicarbonyls formed by splitting of the ring. These dicarbonyls can further get oxidized to polycarbonyls

with or without the hydroxyl groups. FTIR analysis of the oxidization products of 1, 3, 5 Trimethylbenzene shows that the aerosol is formed mostly by ring opening reactions, since the fraction of aromatic species in the particles is only 5–10% (Blando et al., 1998). Organic species in the aerosol phase are highly oxidized and comprised of about three carbonyl groups and one hydroxyl group per average molecule.

The principal reaction pathway giving this 'average molecule' is shown as follows:
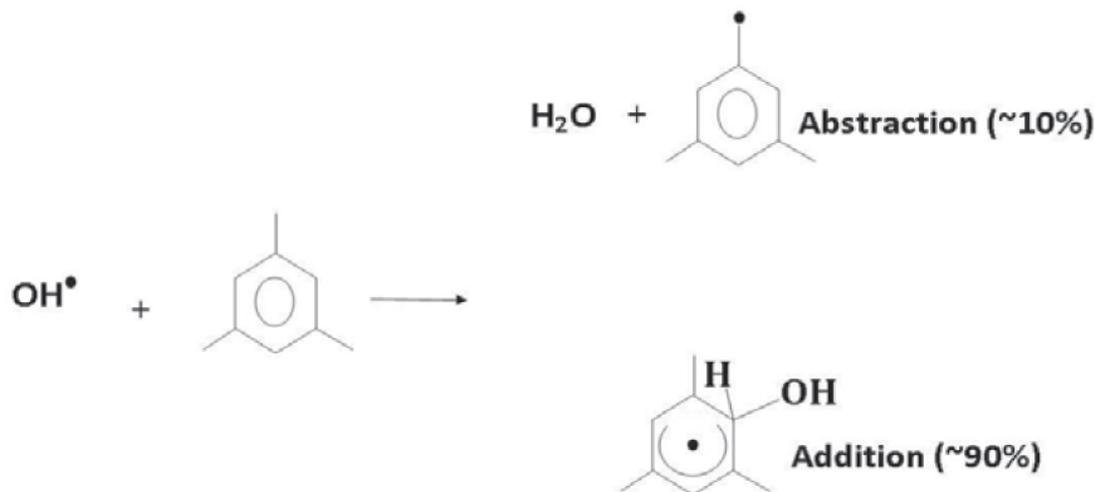
Schematic view of pathway leading to the 'average molecule' in the aerosol phase after oxidation of 1, 3,5–Trimethyl Benzene, (adapted from Blando et al., 1998)

Gas chromatography analysis of the oxidation products of 1, 2, 4 trimethylbenzene produces an equal fraction of ring fragmentation and ring retaining products (Forstner et al., 1997a). Consequently, this analyzable fraction cannot act as a representative of the total organic aerosol produced by the oxidation of trimethylbenzene. Furthermore, a major portion of the known fraction is composed of furandiones that cannot be identified using FTIR spectroscopy. Therefore, it is not obligatory that the pathways prominent for the average molecule are same as that of the real atmospheric oxidation. The difference in the chemistry of 1, 3, 5 and 1, 2, 4 trimethylbenzene can affect the production of SOA composition.

Various studies have proposed that the contribution of absorption in gas to particle conversion in the atmosphere is more than that from

condensation. Smog chamber experiments showed that the aerosol yield depends upon the mass of the organic aerosol produced (Odum et al., 1997, 1996), which could not be possible if condensation had been the dominant gas to particle conversion mechanism. It is very challenging to identify whether adsorption or absorption is the dominant gas to particle conversion mechanism in the atmosphere. Some experimental results have revealed that in urban aerosol absorption is the dominant mechanism.

3.2. Effects of temperature and relative humidity on SOA formation

3.2.1. Temperature

An increase in temperature raises the efficiency for ROGs but at the same time it decreases the partitioning coefficient (Leach et al., 1999). This occurs since all the gas to particle conversion mechanisms follow an inverse relationship with saturation vapor pressure p_0 of the corresponding

SVOC, and p_0 increases exponentially with temperature. As a result SOA formation prefers an optimum temperature at which both effective oxidation and condensation occurs. It has been proposed that this temperature falls in the range of 15°C–20°C (Strader et al., 1999).

According to Strader et al. (1999) the SOA concentration curve attains maxima at 17°C. With increasing engine load, engine exhaust temperature increases consequently the temperature of the diluted exhaust in the photochemical chamber rises with increase in the engine load. Higher chamber temperature aids in oxidation of VOCs into SOC to a certain degree but also results in lower gas to particle conversions if the temperatures are too high. Hence, the oxidation of the VOCs becomes more efficient with increasing engine load (Gupta et al., 2010)

3.2.2. Relative Humidity

Relative humidity affects all the three gas to particle conversion mechanisms. It has been found that in inorganic compounds, water soluble SVOCs can easily nucleate with water vapor nevertheless not much is identified in the case of organic SVOCs (Seinfeld and Pandis, 1998). Rise in relative humidity results in the decrease in the adsorption of SVOCs to particle surfaces, as now they have to compete with a relatively larger number of water molecules for the same number of sorption sites (Story et al., 1995). However, when the particle surface is completely covered with a layer of water then the adsorption of SVOC starts rising again. Differences in humidity can increase or decrease the absorption of SVOCs over the ambient aerosol. There can be variations in the values of activity coefficient for dissolution of SVOCs in dry and wet organic aerosols (Goss and Schwarzenbach, 1998).

The droplet formation potential of a particle also depends on its hygroscopic properties and physical state (solid, liquid, heterogeneous) in addition to the availability of water vapor and temperature of the ambient air. If the absorbing aerosol is liquid then at elevated relative humidity the polar and acidic species will dissolve more easily, than that of non–polar and insoluble compounds and would grow at a faster rate. Typically, smog chamber experiments are carried out at low relative humidity; hence this effect has not been looked in detail in the previous studies. Furthermore, a recent study shows that contribution of diesel vehicles to SOA formation is more prominent in summer, whereas it is dominated by gasoline engines in the winter (Saxena and Hildemann, 1996).

3.3. Oxidation of Reactive Organic Gases (ROGs)

(a) Gas Phase Oxidation: O_3, OH radical and NO_3 radical are the 3 major ambient oxidizing agents. Hydroxyl radical (OH) formed by photolysis of ozone in the presence of moisture. There are compounds (oxygenated aliphatic, saturated aliphatic, aromatics) which are not as reactive and indicate limited activity in presence of OH radicals. O_3 and NO_3 can oxidize double bond containing ROGs. A few of these oxidation products are observed in the particle phase because of their lower vapor pressure such as polyols, dicarboxylic acids, amino acids and other such multifunctional compounds (Rogge et al., 1993; Forstner, 1997a, 1997b; Blando et al., 1998; Limbeck and Puxbaum, 1999; Blando and Turpin, 2000; Ghio et al., 2000).

(b) Liquid Phase Oxidation: Most of the precursor gases emitted by anthropogenic sources are water insoluble nevertheless their hygroscopicity rises with aging. Fogs and clouds being rich in oxidizing agents result in the adsorption of hygroscopic VOCs. Carboxylic acids, glyoxal, esters, and organo sulfur compounds are the common products of fog and cloud processing (Samet et al., 2009). Studies have shown presence of several mono and di–carboxylic acids in the sampled rain water and fog (Abbass et al., 1991; Samet et al., 2009). Formaldehyde can also get collected in the fog droplets (Facchini et al., 1992). A recent study (Aumont et al., 2000) proposed that carboxylic acid formation is mostly dominated by VOC oxidation in the aqueous phase.

4. Health Effects of Diesel particulates and associated with other combustion sources

Numerous acute and chronic studies have critically examined diesel engine exhaust toxicity. Laboratory animals have served as good models and their results have been extrapolated for humans when looking at responses to diesel particulate matter (DPM) (International Life Sciences Institute, 2000; US EPA, 2002). Many studies reported that exposure to diesel exhaust results in acute eye and bronchial irritation, nausea, lightheadedness, phlegm and cough.

In addition, a number of chronic studies involving laboratory rats, mice, and monkeys, have been conducted recently to monitor the respiratory as well as systemic effects when exposed to DPM (Diaz–Sanchez et al., 1996). Acute exposures to very high concentrations of raw diesel exhaust cause respiratory inflammation. Also, the nasal deposition of extremely high doses of diesel exhaust PM enhances the immunological responses to various ambient antigens. Lifetime exposures of lab animals to elevated concentrations of DPM have shown to cause chronic inflammation and fibrosis. The semi–volatile and soot borne organic material has been clinically shown to be mutagenic both to animal skin and respiratory tract. In one of the studies, the nasal instillation of a diesel exhaust aerosol in a group of human subjects lead to increase of local immunoglobulin E (IgE) and cytokine responses to antigen (Diaz–Sanchez et al., 1997; Diaz–Sanchez et al., 1999; Ghio et al., 2000). Organic fraction of diesel exhaust has been associated chiefly for their observed health response in the test population (Ghio and Huang, 2004).

In addition to diesel exhaust, various other sources of ultrafine particles include tobacco smoke; welding fumes, smoke from cooking stoves running on biomass or kerosene, and thermal power plants. Insoluble nanoparticles, their large surface area provides ample scope for catalytic reactions that results in the formation of (ROS) free radicals that are responsible for oxidative stress, inflammation and apoptosis. Huge surface areas of the nanoparticles which provide enormous adsorption sites for toxic species like PAHs to attach are correlated very well with their toxic effects.

Healthy human volunteers exposed for a short period to concentrated ambient particles (Blando et al., 1998), showed varied health effects. Simultaneous chemical speciation followed by PCA leads to interesting conclusions. A few studies have also supported acute effect of the short–term exposure to high level of PM and ozone on our systemic circulation system. Adverse health effects have been identified even for healthy individuals who are exposed to enormously large number of ultrafine particles under controlled exposure (Gupta et al., 2004). Daily individuals get exposed to combustion generated products either indoors (home, occupational settings) or outdoors (traffic, field work). However, few of them only respond to their high levels of air pollutants. This anomaly may be explained by the differences inherently present between individuals due to their health conditions, age and genetic variation.

5. Conclusions

The main goal of this review was to provide an overview on the current state of knowledge combustion generated organics and to summarize the key characteristics of these organic species as well as their impacts on the human health. Organic compounds form a major fraction of airborne particles and hence it is significant to measure and identify the organic contaminants and especially the PAHs and SOA proportion emitted primarily from the different combustion sources. The control and abatement of theses organic residues requires the knowledge of the nature, source, and extent of pollution and hence existing literature has been reviewed to synthesize the available information on the formation, sources of these organic compounds. This review provides researchers with a holistic picture of this grave issue and provides ample proof for implementation of policy related initiatives and interventions.

References

1. Abbass, M.K., Andrews, G.E., Williams, P.T., and Bartle, K.D., 1991. The influence of diesel fuel composition on particulate PAH emissions. SAE Paper No. 892079.

2. Agarwal, A.K., Gupta, T., Kothari, A., 2011. Particulate emissions from biodiesel vs diesel fuelled compression ignition engine. Renew. Sustain. Energ. Rev. 15, 3278–300.

3. Agarwal, A.K., Gupta, T., Dixit, N., Shukla, P.C., 2013. Assessment of toxic potential of primary and secondary particulates/aerosols from biodiesel vis–a–vis mineral diesel fuelled engine. Inhal. Toxicol. 25, 325–332.

4. Agarwal, A.K., Gupta, T., Shukla, P.C. Dhar, A., 2015. Particulate emissions from biodiesel fuelled CI engines. Energ. Convers. Manage. 94, 311–330.

5. Aumont, B., Madronich, S., Bey, I., Tyndall, G.S., 2000. Contribution of secondary VOC to the composition of aqueous atmospheric particles: A modeling approach. J. Atmos. Chem. 35, 59–75.

6. Ballesteros, R., Hernandez, J., Lyons, L., Cabanas, B., Tapia, A., 2008. Speciation of the semivolatile hydrocarbon engine emissions from sunflower biodiesel. Fuel 87, 1835–1843.

7. Barbella, G.T., 1988. Soot and unburnt liquid hydrocarbon emissions from diesel engines. Combust. Sci. Technol. 59, 183–198.

8. Baumgard, K.J., Johnson, J.H., 1992. The effect of low sulfur fuel and a ceramic particle filter on diesel exhaust particle size distributions. SAE Transactions 101, 691–699.

9. Bergmann, M., Kirchner, U., Vogt, R., Benter, T., 2009. On–road and laboratory investigation of low–level PM emissions of a modern diesel particulate filter equipped diesel passenger car. Atmos. Environ. 43, 1908–1916.

10. Bildeman, T.F., 1988. Atmospheric Process. Environ. Sci. Technol. 22, 361–367.

11. Blando, J.D., Porcja, R.J., Li, T.H., Bowman, D., Lioy, P.J., Turpin, B.J., 1998.

Secondary formation and the Smoky Mountain organic aerosol: An examination of aerosol polarity and functional group composition during SEAVS. Environ. Sci. Technol. 32, 604–613.

12. Blando, J.D., Turpin, B.J., 2000. Secondary organic aerosol formation in cloud and fog droplets: a literature evaluation of plausibility. Atmos. Environ. 34, 1623–1632.

13. Cass, G.R., Hughes, L.A., Bhave, P., Kleeman, M.J., Allen, J.O., Salmon, L.G., 2000. The chemical composition of atmospheric ultrafine particles. Philos. Trans. R. Soc. Lond. A Math. Phys. Sci. 358, 2581–2592.

14. Cheung, C., Zhu, L., Huang, Z., 2009. Regulated and unregulated emissions from a diesel engine fueled with biodiesel and biodiesel blended with methanol. Atmos. Environ. 43, 4865–4872.

15. Dhar, A., Agarwal, A.K., 2013. Effect of multiple injections on particulate size–number distributions in a common rail direct injection engine fueled with karanja biodiesel blends. SAE Technical Paper 2013–01–1554.

16. Di, Y., Cheung C, Huang Z., 2009. Experimental investigation on regulated and unregulated emissions of a diesel engine fueled with ultra–low sulfur diesel fuel blended with biodiesel from waste cooking oil. Sci. Total Environ. 407, 835–846.

17. Diaz, E.A., Chung, Y., Papapostolou, V., J. Lawrence, M.S. Long, V., Hatakeyama, B., Gomes, Y., Calil, Sato, R., Koutrakis, P., 2012. Effects of fresh and aged vehicular exhaust emissions on breathing pattern and cellular responses–pilot single vehicle study, Inhal. Toxicol. 24, 288–295.

18. Diaz–Sanchez, D., Tsien, A., Casillas, A., Dotson, A.R., and Saxon, A., 1996. Enhanced nasal cytokine production in human beings in vivo challenge with diesel exhaust particles. J. Allergy Clin. Immunol. 98, 114–123.

19. Diaz–Sanchez, D., 1997. The role of diesel exhaust particles and their associated polyaromatic hydrocarbons in the induction of allergic airway disease. Allergy, 52 (38 suppl.), 52–56.

20. Diaz–Sanchez, D., Garcia, M.P., Wang, M., Jyrala, M., and Saxon, A., 1999. Nasal challenge with diesel exhaust particles can induce sensitization to a neoallergen in the human mucosa. J. Allergy Clin. Immunol. 104, 1183–1188.

21. Dusek, U., Amann, M., 2000. Secondary Organic Aerosol–Formation Mechanisms and Source Contributions in Europe. IIASA Interim report IR–00–066.

22. Eastwood, P., 2008. Particulate emissions from vehicles, John Wiley & Sons.

23. Facchini, M. S., Fuzzi, J. Lind, H.F.O., Kalina, M. H., Puxbaum, W. Winiwarter, B., Arends, W., Wobrock, W., Jaeschke.,1992. Phase partitioning and chemical reactions of low molecular weight organic compounds in fog. Tellus B, 44, 533–544.

24. Fenger, J., 2009. Air pollution in the last 50 years from local to global. Atmos. Environ. 43, 13–22.

25. Flynn, P.F., Durrett, R.P., Hunter, G.L., zur Loye, A.O., Akinyemi, O. Dec, J.E, et al., 1999. Diesel combustion: an integrated view combining laser diagnostics, chemical kinetics, and empirical validation. SAE Technical Paper 1999–01–0509.

26. Forstner, H.J., Flagan, R.C., Seinfeld, J.H., 1997a. Secondary organic aerosol from the photooxidation of aromatic hydrocarbons: Molecular composition. Environ. Sci. Technol. 31, 1345–1358.

27. Forstner, H.J., Flagan, R.C., Seinfeld J.H., 1997b. Molecular speciation of secondary organic aerosol from photooxidation of the higher alkenes: 1–octene and 1–decene, Atmos. Environ., 31, 1953–1964.

28. Ghio, A.J., Kim, C., Devline, R.B., 2000.Concentrated ambient particles induce mild pulmonary inflammation in healthy human volunteers. Am. J. Respir. Crit. Care Med. 162, 981–988.

29. Ghio, A.J., Huang, Y.C.T., 2004. Exposure to concentrated ambient particles (CAPs): a review. Inhal. Toxicol. 16, 53–59.

30. Godlee, F. 1993. Air pollution II: road traffic and modern industry. Br. Med. J. 303, 1539–1543.

31. Goss, K.–U., Schwarzenbach, R. P., 1998. Gas/Solid and Gas/Liquid partitioning of organic compounds: Critical evaluation of equilibrium constants. Environ. Sci. Technol. 32, 2025–2032.

32. Grosjean, D., Seinfeld, J.H., 1989. Parameterization of the formation potential of secondary organic aerosols. Atmos. Environ. 23, 1733–1747.

33. Grosjean, D., Grosjean, E., Gertler, A.W., 2001. On–road emissions of carbonyls from light–duty and heavy–duty vehicles. Environ. Sci. Technol. 35, 45–53.

34. Gupta, T., Demokritou, P., Koutrakis, P., 2004. Development and evaluation of an ultrafine particle concentrator for inhalation toxicological studies. Inhal. Toxicol. 16, 851–862.

35. Gupta, T., Kothari, A., Srivastava ,D.K., Agarwal, A.K., 2010. Measurement of number and size distribution of particles emitted from a mid–sized transportation multipoint port fuel injection gasoline engine, Fuel, 89, 2230–2233.

36. Gupta, T., Agarwal, A.K., 2010. Toxicology of Combustion Products Handbook of Combustion Vol.1: Fundamentals and Safety. Edited by Maximilian Lackner, Franz Winter, and Avinash . Agarwal Copyright WILEY–VCH Verlag GmbH & Co. KGaA, Weinheim ISBN: 978–3–527–32449–1357–377.

37. Ho, S.S.H., Ho, K.F., Lee, S.C., Cheng, Y., Yu., J.Z, Lam, K.M, et al. 2012. Carbonyl emissions from vehicular exhausts sources in Hong Kong. J. Air Waste Manag. Assoc. 62, 221–34.

38. Holes, A., Eusebi, A., Grosjean, D., Allen, D.T., 1997. FTIR analysis of aerosol formed in the photooxidation of 1, 3, 5–trimethylbenzene. Aerosol Sci. Technol. 26, 516–526.

39. Honda, T., 1984. In–situ emission levels of carcinogenic and mutagenic compounds from diesel and gasoline engine vehicles on an express way. Environ. Sci. Technol. 18, 895–902.

40. Hyslop, N.P., 2009. Impaired visibility: the air pollution people see. Atmos. Environ. 43, 182–195.

41. International Life Sciences Institute (ILSI), 2000. The relevance of the rat lung response to particle overload for human risk assessment, in ILSI Risk Science Institute Workshop, vol. 12 (1–2) (ed. D.E. Gardner), Inhalation Toxicology, pp. 1–148.

42. Jacobson, M., Hansson, H.C., Noone, K., Charlson, R., 2000. Organic atmospheric aerosols: Review and state of the science. Rev. Geophys. 38, 267–294.

43. Jaidevi, J., Tripathi, S.N., Gupta, T.B., Singh, N., Gopalakrishnan, V., Dey, S., 2011. Observation–based 3–D view of aerosol radiative properties over Indian Continental Tropical Convergence Zone: Implications to regional climate, Tellus, 63B, 971–989.

44. Jensen, T.E., Hites, R.A., 1983. Aromatic diesel emissions as a function of engine condition. Anal. Chem., 55, 594–599.

45. Johnson, J.H., Bagley, S.T., Gratz, L.D., Leddy, D.G., 1992. A review of diesel particulate control technology and emissions effects. SAE Paper No. 940233.

46. Karavalakis, G., Stournas, S., Bakeas, E., 2009. Effects of diesel/biodiesel blends on regulated and unregulated pollutants from a passenger vehicle operated over the European and the Athens driving cycles. Atmos. Environ. 43, 1745–1752.

47. Kaul, D., Gupta, T., Tripathi, S.N., Tare, V., Collett, Jr J., 2011. Secondary organic aerosol: a comparison between foggy and nonfoggy days, Environ. Sci. Technol. 45, 7307–7313.

48. Khair, M.K., Majewski, W.A., 2006. Diesel emissions and their control, in, SAE Technical Paper.

49. Kittelson, D.B., 1985. Measurements of PAH in the cylinders of an operating diesel engine. EPA Report No. 600/D–85/ 012.

50. Kittelson, D.B., 1998. Engine and nanoparticles: a review. J. Aerosol Sci. 29, 575–588.

51. Krahl, J., Munack, A., Ruschel, Y., Schröder, O., Bünger J., 2008. Exhaust gas emissions and mutagenic effects of diesel fuel, biodiesel and biodiesel blends. SAE Technical Paper 2008–01–2508.

52. Krahl, J., Munack, A., Schröde, O., Stein, H., Bünger, J., 2003. Influence of biodiesel and different designed diesel fuels on the exhaust gas emissions and health effects. SAE Technical Paper, 2003–01–3199.

53. Kristensson, A., Johansson, C., Westerholm, R., Swietlicki, E., Gidhagen, L., Wideqvist, U., et al. 2004.Real–world traffic emission factors of gases and particles measured in a road tunnel in Stocholm, Sweden. Atmos. Environ. 38, 657–673.

54. Leach, K. B., Kamens, R. M., Strommen, M. R., Jang, M., 1999. Partitioning of semivolatile organic compounds in the presence of a secondary organic aerosol in a controlled atmosphere. J. Atmos. Chem. 33, 241–264.

55. Lea–Langton, A., Li, H., Andrews, G.E., 2008. Comparison of particulate PAH emissions for diesel, biodiesel and cooking oil using a heavy duty DI diesel engine. SAE Technical Paper 2008–01–1811.

56. Liaquat, A.M., Kalam, M.A., Masjuki, H.H., Jayed, M.H., 2010. Potential emissions reduction in road transport sector using biofuel in developing countries. Atmos. Environ. 44, 3869–3877.

57. Limbeck, A., Puxbaum, H., 1999. Organic acids in continental background aerosols. Atmos. Environ. 33, 1847–1852.

58. Liu, Y.Y., Lin, T.C., Wang, Y.J., Ho, W.L., 2009. Carbonyl compounds and toxicity assessments of emissions from a diesel engine running on biodiesels. J. Air Waste Manage. Assoc. 59, 163–171.

59. Loeffler, K.W., Koehler, C.A., Paul, N.M., De, Haan, D.O., 2006.Oligomer formation in evaporating aqueous glyoxal and methyl glyoxal solutions. Environ. Sci. Technol. 40, 6318–6323.

60. Machado, C. S., Arbilla, G, 2008. Carbonyl emissions in diesel and biodiesel exhaust. Atmos. Environ. 42, 769–775.

61. Madden, M.C., Dailey, L.A., Stonehuerner, J.G, Harris, D.B., 2003. Responses of cultured human airways epithelial cells treated with diesel exhaust extracts will vary with the engine load. J. Toxicol. Environ. Health A 66, 2281–2297.

62. McDonald, J.D., Barr, E.B., White, R.K., Chow, J.C., Schauer, J.J., Zielinska, B., et al. 2004. Generation and characterization of four dilutions of diesel engine exhaust for a subchronic inhalation study. Environ. Sci. Technol. 38, 2513–2522.

63. National Research Council., 1999. Automotive fuel economy, National Research Council Committee on Fuel Economy of Automobiles and Light Trucks, Energy Engineering Board, National Academy Press, Washington, DC.

64. Nisbet, I.C., LaGoy, P.K., 1992. Toxic equivalency factors (TEFs) for polycyclic aromatic hydrocarbons (PAHs). Regul. Toxicol. Pharmacol. 16, 290–300.

65. Odum, J. R., Hoffmann, T., Bowman, F., Collins D., Flagan, R. C., Seinfeld J. H., 1996. Gas/Particle partitioning and secondary organic aerosol yields. Environ. Sci. Technol. 30, 2580–2585.

66. Odum, J. R., Jungkamp, T. W. P., Griffin, R. J., Flagan, R. C., Seinfeld J. H., 1997.The atmospheric aerosol formation potential of whole gasoline vapor. Science 274, 96–99.

67. Opris, C.N., Gratz, L.D., Bagley, S.T., Baumgard, K.J., Leddy, D.G., and Johnson, J.H., 1993. The effects of fuel sulfur concentration on regulated and unregulated heavy–duty diesel emissions. SAE Paper No. 930733.

68. Pan, J., Quarderer, S., Smeal, T., Sharp, C., 2000. Comparison of PAH and nitro–PAH emissions among standard diesel fuel, biodiesel fuel, and their blend on diesel engines. In: Proceedings of the 48th ASMS conference on mass spectrometry and allied topics, Long Beach, CA.

69. Pang X, Shi X, Mu Y, He H, Shuai S, Chen H, et al. 2006. Characteristics of carbonyl compounds emission from a diesel–engine using biodiesel–ethanol–diesel as fuel. Atmos. Environ. 40, 7057–65.

70. Ramanathan, V., Feng, Y., 2009. Air pollution, greenhouse gases and climate change: global and regional perspectives. Atmos. Environ. 43, 37–50.

71. Ravindra, K., Sokhi, R., Van Grieken, R., 2008. Atmospheric polycyclic aromatic hydrocarbons: source attribution, emission factors and regulation. Atmos. Environ. 42, 2895–2921.

72. Robinson, A.L., Donahue, N.M., Shrivastava, M.K., Weitkamp, E.A., Sage, A.M., Grieshop, A.P., Lane, T.E. Pierce, J.R., Pandis, S.N., 2007. Rethinking organic aerosols: Semivolatile emissions and photochemical aging. Science, 315, 1259–1262.

73. Rogge, W.F., Hildemann, L.M., Mazurek, M.A., and Cass, G.R., 1993a. Sources of fine organic aerosol II: Noncatalyst and catalyst–equipped automobiles and heavy–duty diesel trucks. Environ. Sci. Technol., 27, 636–651.

74. Rogge, W.F., Mazurek, M.A., Hildemann, L.M., Cass, G.R., Simoneit, B.R., 1993b. Quantification of urban organic aerosols at a molecular level: identification, abundance and seasonal variation. Atmospheric Environment. Part A. General Topics, 271309–1330.

75. Ruckerl, R., Schneider, A., Breitner, S., Cyrys, J., Peters, A., 2011. Health effects of Particulate air pollution a review of epidemiological evidence. Inhal. Toxicol. 23, 555–592.

76. Samet, J.M., Rappold, A., Gaff, D., Cascio, W.E., Berntsen, J.H., Huang, Y.C.T., Herbst, M., Bassett, M., Montilla, T., Hazucha, M.J., Bromberg, P.A., Devlin, R.B., 2009. Concentrated ambient ultrafine particle exposure induces cardiac changes in young healthy volunteers. Am. J. Respir. Crit. Care Med., 179, 1034–1042.

77. Saxena, P., Hildemann, L.M., 1996. Water–soluble organics in atmospheric particles: A critical review of the literature and application of thermodynamics to identify candidate compounds. J. Atmos. Chem. 24, 57–109.

78. Schauer, J.J., Kleeman, M.J, Cass, G.R., Simoneit, B.R., 1999. Measurement of emissions from air pollution sources. 2. C1 through C30 organic compounds from medium duty diesel trucks. Environ. Sci. Technol. 33, 1578–1587.

79. Schauer, J.J., Kleeman, M.J., Cass, G.R., Simoneit, B.R., 2002. Measurement of emissions from air pollution sources. 5. C1–C32 organic compounds from gasoline powered motor vehicles. Environ. Sci. Technol. 36, 1169–1180.

80. Schroeder, O., Krahl, J., Bünger, J., 1999. Environmental and health effects caused by the use of biodiesel. SAE Technical Paper 1999–01–3561.

81. Schuetzle, D. and Frazier, J.A., 1986. Factors influencing the emission of vapor and particulate phase components from diesel engines, in Carcinogenic and Mutagenic Effects of Diesel Engine Exhaust (eds N. Ishinishi, A. Koizumi, R.O. McClellan, and W. St•ober), Elsevier Science Publishers, pp. 41–63.

82. Seinfeld, J. H. and Pandis, S. N., 1998. Atmospheric Chemistry and Physics: From Air Pollution to Climate Change, John Wiley & Sons, New York.

83. Seinfeld, J.H., and Pandis, S.N. 2012. Atmospheric chemistry and physics: from air pollution to climate change, John Wiley & Sons,

84. Singh, D.K., Sharma, S., Habib, G., Gupta, T., 2015. Speciation of atmospheric polycyclic aromatic hydrocarbons (PAHs) present during fog time collected submicron particles. Environ. Sci. Pollut. Res. 22, 12458–12468.

85. Story, J.M., Luo, W, Isabelle, L. M., Pankow, J.F., 1995. Gas/solid partitioning of semi–volatile organic compounds to model atmospheric solid surfaces as a function of relative humidity. Environ. Sci. Technol. 29, pp. 2420–2428.

86. Strader, R., Lurmann, F., Pandis, S. N., 1999. Evaluation of secondary organic aerosol formation in winter. Atmos. Environ. 33, 4849–4863.

87. Takada, K., Yoshimura, F., Ohga, Y., Kusaka, J., Daisho, Y., 2003. Experimental study on unregulated emission characteristics of turbocharged DI diesel engine with common rail fuel injection system. SAE Technical Paper 2003–01–3158.

88. Tobias, H.J., Beving, D.E., Ziemann, P.J., Sakurai, H., Zuk, M., Mc Murry, P.H., Zarling, D., Waytulonis, R., and Kittelson, D.B., 2001. Chemical analysis of diesel engine nanoparticles using a nano–DMA/thermal desorption particle beam mass spectrometer. Environ. Sci. Technol. 35, 2233–2243.

89. Turpin, B.J., Saxena, P., Andrews, E., 2000. Measuring and simulating particulate organics in the atmosphere: problems and prospects. Atmos. Environ. 34, 2983–3013.

90. U.S. Environmental Protection Agency, 2002. Health assessment document for diesel engine exhaust. EPA Report No. 600/8–90–057F.

91. Watt, J., Tidblad, J., Kucera, V., Hamilton, R. (Eds.), 2009. The Effects of Air Pollutionon Cultural Heritage. Springer, New York, p. 306.

92. Westerholm, R., Li, H., 1994. A multivariate statistical analysis of fuel related polycyclic aromatic hydrocarbon emissions from heavy–duty diesel vehicles. Environ. Sci. Technol. 28, 965.

93. Xue, J., Grift, T.E., Hansen, A.C., 2011. Effect of biodiesel on engine performances and emissions. Renew. Sustain. Energ. Rev.15, 1098–10116.

94. Yang, W., Omaye, S.T., 2009. Air pollutants, oxidative stress and human health. Mutat. Res. 674, 45–54.

95. Zielinska, B., 2005. Atmospheric transformation of diesel emissions. Exp. Toxicol. Pathol. 57, 31–42.