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The Secondary Organic Carbon (SOC) Formation from a CRDI Automotive Diesel Engine Exhaust

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ABSTRACT

Condensed soot coming out of vehicular exhaust is commonly classified as organic carbon (OC) and elemental carbon (EC). OC can be directly emitted to the atmosphere in the particulate form (primary carbon) from the tailpipe or can be produced by gas-to-particle conversion process (secondary organic carbon, SOC). Under typical atmospheric dilution conditions, most of the semi-volatile material is present in the form of soot. SOC holds wider implications in terms of their adverse health and climate impact. Diesel exhaust is environmentally reactive and it has long been understood that the ambient interaction of exhaust hydrocarbons and NO_x results in the formation of ozone and other potentially toxic secondary organic carbon species.

The current emission norms look at the primary emissions from the engine exhaust. Also, research efforts are geared towards controlling the emissions of primary carbon. However the secondary organic carbon produced as a result of gas-to-particle conversion upon mixing of gaseous tailpipe emissions with the ambient air in presence of sunlight is also of significant importance. Therefore evaluation of gaseous emissions from engine exhausts using an artificial photochemical chamber mimicking the atmospheric conditions can serve as an important tool to assess the potential adverse health impact of secondary engine emissions. A modern common rail direct injection engine has been chosen as the emission source for the current investigation using mineral diesel. The main objective of this study was to look at the ratio or percentage change between the primary and secondary tailpipe emissions with focus on SOC using diesel fuel at different engine load conditions using an optimized photochemical chamber. Through these experiments, an attempt has been made to investigate the SOC yield from diesel fuelled CRDI engine under fairly moderate ageing conditions for different load conditions at rated engine speed. The ageing of exhaust emission was done for RH varying from 40-60% and temperature range of 35-40°C. Primary emissions of OC, EC and PAHs increased in diesel exhaust with increasing engine load. With increase in engine load, rate of primary EC emission is higher than rate of increase of OC emissions. Particle bound PAHs increases by an order of magnitude after ageing, which indicates that the toxic potential of diesel engine exhaust might increase an order of magnitude even under moderate ageing conditions.

INTRODUCTION

Atmospheric radiative balance gets disturbed due to attenuation of light by the atmospheric fine particles (diameter < 2.5 μm) [1]. In fact, finer the particles, higher the interaction it has with the visible spectrum of light. Chemical composition wise, fine particles emitted from diesel engines have three major components, which result in attenuation of light namely EC, OC and sulphates. EC causes atmospheric warming due to absorption of light, whereas OC and sulphates cause atmospheric cooling by scattering the light. In addition, fine particles get transported to long distances away from their emission sources. Their surface properties and affinity towards water make these tiny particles excellent sites for water condensation and hence they have an indirect climatic impact in the form of modification of cloud micro-physical properties [2].

Ultrafine particles emitted from diesel engines have been detected in deeper parts of lungs as well as in blood stream shortly after controlled animal exposure experiments [3]. Research has estimated the average annual human exposure to diesel exhaust in different urban settings to be in the range of 1-4 $\mu g/m^3$ of inhaled air [4]. Numerous studies suggested

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that diesel exhaust exposure causes acute eye and bronchial irritation, nausea, lightheadedness, phlegm and cough. The semi volatile and soot-borne organic material of the diesel exhaust is mutagenic and an inhalation exposure of rats to high concentrations of it has resulted in lung tumors. There is also some evidence for possible immunologic effects and exacerbation of allergenic response to known allergens due to synergistic effect with diesel exhaust. It has also been shown that this activity is primarily due to the organic fraction of diesel exhaust [5]. Laboratory toxicological studies have revealed that the SOF portion is largely responsible for tumor formation [6, 7, 8, 9]. Polycyclic aromatic hydrocarbons (PAHs) have a significant contribution to the overall carcinogenic effect [10, 11, 12].

Diesel exhaust emissions also contribute towards several regional and global environmental effects. Regional environmental effects such as acid rain and smog are a result of complex photochemical reactions and formation of secondary particles from several aldehydes and ketones, carbon monoxides, nitrogen oxides emitted in gaseous form from the tailpipes of diesel engines. CO_2, CO, methane, non-methane hydrocarbons, nitrous oxide also contribute towards the global warming [13, 14, 15].

DIESEL EXHAUST

Diesel exhaust is a complex mixture of gases and fine particles. The gaseous components of diesel exhaust are similar to the combustion products of other fuels. Although the adverse effects of diesel emissions are due to both the gaseous and particulate components, the toxicity of diesel exhaust is often related to its particulates [16]. Several agencies have classified diesel exhaust as a carcinogen and composition of diesel particulates varies with engine type, operating conditions, fuel and lubricating oil composition [17, 18, 19]. Diesel exhaust particles (particulates) are aggregates of primary spherical particles that consist of solid carbonaceous material and ash with associated adsorbed material. The particle portion of diesel exhaust contains EC, OC, traces of sulphates, nitrates, heavy metals, other trace elements, water, and some unidentified compounds. Elemental carbon usually makes up 50-75% and organic carbon makes up 19-43% of the particles in the exhaust [20]. OC emanating from modern diesel engines is formed primarily from partial combustion and pyrolysis products, with a little amount contributed by unburned fuel and lubricating oil. Several previous studies have looked at fuel changes, such as reduced aromatic content (higher cetane number), reduced fuel sulfur, increased fuel volatility, and decreased fuel density [17, 18, 19, 20, 21]. A significant reduction in emissions has been reported by studies using oxygenated diesel fuels [21]. PAHs make up less than 1% of diesel exhaust particle mass. Carbonaceous matter refers to all carbon-containing compounds in diesel particles, and includes the EC and OC. Elementally; OC is made up of carbon and hydrogen [22]. It has been shown that atmospheric photochemical reactions of vehicular emissions can result in the formation of secondary organic aerosols, as well as in the alteration of the toxicity and mutagenicity of PAHs, most probably via the formation of nitro- or oxy-PAH derivatives. Photochemical chambers are valuable tools for performing emission ageing experiments in a controlled environment.

SECONDARY ORGANIC CARBON

Ambient aerosols comprise of EC, OC and inorganic ionic species such as ammonium, nitrates, chlorides and sulfates [23]. The aerosols are classified as primary or secondary. The respective sources such as diesel engines emit the primary particles while the secondary aerosols are formed in atmosphere as a result of condensation of gaseous precursors. The concentration of aerosol particles and increased rate of morbidity have a definite correlation. It has been proven by epidemiological evidence and rate of mortality. The mechanism due to which, these ambient particles are harmful to human health is still a subject matter of research [24]. Analytical methods currently used are not up to the mark for evaluating the organic fraction to composition of many individual species in SOC. The oxidation of Volatile Organic Carbon (VOC) leads to the formation of SOC [25]. The composition of SOC and its formation mechanism needs to be studied to be able to reduce SOC or devise tools for their effective control. VOC precursor gases are mainly oxidized by O_3, NO_3 and OH radicals. Their vapour pressure gets lowered as a result of oxidation of their VOC precursors. A significant fraction of fine mode particles are formed as a result of gas-to-particle conversion [26-27].

Gas-to-particle conversion involved (i) condensation, (ii) absorption and (iii) adsorption.

1. Condensation is the most simple gas-to-particle conversion process as it does not involve the interaction of existing aerosol phase with the condensing gases. A single SVOC species can condense by homo-molecular nucleation, whereas two or more organic species can condense through hetero-molecular nucleation [26].

2. Gas-to-particle conversion by absorption and adsorption involves interaction of the SVOC with the pre-existing aerosols. Absorption is the dominating mechanism, if organic particles are already present in the atmosphere. Organic vapours can dissolve into the pre-existing organic aerosol and represent bulk transfer. Several prior studies have shown that gas-to-particle conversion occurs in the ambient atmosphere dominantly by sorption processes rather than by condensation [28-29].

3. Adsorption is the primary mechanism for uptake of inorganic gases on the surfaces of existing ambient aerosols. This happens at gas phase concentrations much lower than

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required for homo-molecular condensation. Adsorption transfers a fraction of the organic vapour to the particle phase when the gas phase is still under-saturated [25]. Knowledge concerning the products of chemical transformation of diesel exhaust in the air is still limited. Secondary aerosols such as nitro-arenes, nitrates and sulphates from diesel engine exhaust may also exhibit different biological toxicity than the primary particles. There is evidence that reaction of PAHs in the exhaust with nitrogen oxides will form nitro-arenes that are often more mutagenic than their precursors. PAHs are products of both incomplete combustion and pyrolysis of fuel and/ or lubricant. After being emitted, diesel particles undergo ageing (oxidation, nitration or other chemical and physical changes) in the atmosphere. The atmospheric lifetime of the various compounds found in diesel exhaust ranges from hours to days [14]. Particles that are smaller than 1 micron can remain in the atmosphere for up to 15 days [20]. The more reactive compounds with short atmospheric lifetimes will undergo rapid transformation in the presence of the appropriate reactants, whereas more stable pollutants can be transported over greater distances.

It has been shown that atmospheric photochemical reactions of vehicular emissions can result in the formation of secondary organic aerosol, as well as in the alteration of the toxicity and mutagenicity of PAHs [30]. Particles are removed from the atmosphere through dry or wet deposition of the particles. Particles of small diameter (< 1 μm) are removed less efficiently therefore they have longer atmospheric residence times. Because of their small size, diesel exhaust particles have atmospheric residence time in air of several days, and they may be potentially transported over long distances. Gaseous diesel exhaust will primarily react with sunlight, the hydroxyl radical (OH), ozone, the hydroperoxyl radical (HO_2), various oxides of nitrogen and sulphuric acid. Reaction with the OH radical is the major removal route for PAHs in the vapour phase [31] and occurs within a few hours of daylight. In presence of oxides of nitrogen, this oxidation reaction can lead to the formation of nitro-arenes or nitro-PAHs [32]. Oxides of nitrogen (primarily NO) that are emitted in diesel exhaust are also oxidized in the atmosphere to form nitrogen dioxide (NO_2) and nitrates. High molecular weight PAHs in particulates are generally more resistant to atmospheric reactions than PAHs in the vapour phase, leading to an anticipated half-life of one or more days. PAHs undergo photolysis, nitration, and oxidation in presence of sunlight. Diesel engines emit nano-particles that undergo nucleation, coagulation and condensation while coming out of the tailpipe [10]. The volatile reactive organic gases (ROGs) get oxidized to form semi-volatile organic carbon (SVOC) and subsequently these SVOCs partition to the aerosol phase as shown in Figure 1. High vapour pressures of ROGs and slow oxidation of SVOCs can significantly slow down and limit the formation of the secondary organic carbon [25, 33-34].

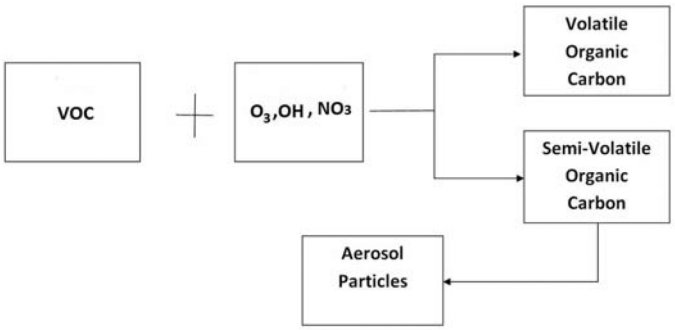

Figure 1. Overview of secondary organic carbon formation.

EXPERIMENTAL SETUP

An experimental setup was developed which included an artificial photochemical chamber along with a set of different instruments like semi continuous OC/ EC analyzer (Make: Sunset Laboratory, USA; Model: Semi-continuous field v.4), which measures organic carbon, elemental carbon and total carbon [35]; Online PAH analyzer (Make: EcoChem Labs, USA; Model: PAS 2000) [36], which measures total particulate bound PAHs for primary as well as secondary aerosols; condensation particle counter (CPC) (Make: TSI Inc., USA; Model: 3007), which measures particle concentration for primary as well as secondary aerosols; and temperature and relative humidity (RH) sensor (Make: Testo, Germany; Model: 605H1) for the photochemical chamber. The emission source of diesel exhaust was a modern diesel engine, which was using common rail direct injection (CRDI) technology for fuel injection at very high injection pressure of the order of 1600 bar. The diesel engine (Make: Tata, India; Model: Safari DICOR 3.0 L) uses a high pressure fuel pump and a common rail for supply of fuel to all cylinders at very high pressures. The injectors were controlled electronically using electronic control unit (ECU). High fuel injection pressure results in better atomization, which leads to more complete combustion, higher efficiency and lower emissions. The engine is coupled with an eddy current dynamometer for loading the engine at different speeds. The dynamometer can be controlled using the dynamometer controller as well as computer with software interface between the dynamometer and the computer. The specifications of the engine and dynamometer used in the experimental setup are given in Table 1.

Experimental setup for this study is shown in Figure 2. Exhaust flow through chamber inlet, outlet and different instrument inlets are shown in the figure. Experimental setup was developed using pipes, elbows and valves (Swagelok fittings) made of stainless steel (SS, grade 316), in order to ensure minimum contamination during experiment due to the inert nature of SS. Valves were installed at different places to control and distribute required exhaust aerosol flows to the

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Table 1. Engine and eddy current dynamometer specifications.

Engine Specifications	
Make/ Model	Tata, India/ Safari Dicor 3.0 L (BS-III/ Euro-III)
Engine Type	Water cooled, CRDI, Turbocharged, Intercooled
No. of Cylinders	4, In-line
Bore/ Stroke	97/ 100 mm
Cubic Capacity	2956 cc
Maximum Engine Output	84.5 kW @ 3000 rpm
Maximum Torque	300 Nm at 1600-2000 rpm
Compression Ratio	17.5
Firing Order	1-3-4-2
Fuel Injection System	CRDI with 1600 bar max fuel injection pressure
Timing and Governing	ECU control
Dynamometer Specifications	
Make/ Model	Dynomerk, Pune, India/ EC-300
Capacity	220 KW at 2500-8000 rpm
Maximum Speed	8000 rpm
Maximum Torque	702 Nm
Direction Of Rotation	Bi-directional
RPM Accuracy	±1 rpm

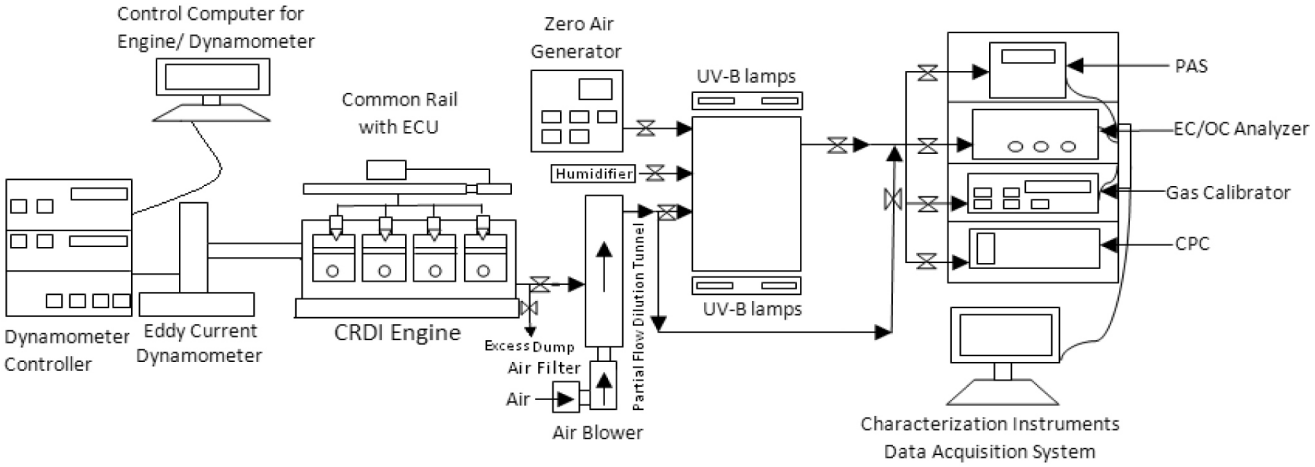

Figure 2. Experimental setup.

instruments at different times of experiment, for sampling either primary or secondary aerosol at a given time according to the measurement requirements. All the instruments were calibrated and tested individually with ambient air before carrying out the engine experiments.

Before starting the experiment, zero air supply was utilized to flush the photochemical chamber. Zero air supply uses an external compressor, a pressure regulators, chemical scrubbers, a reactor and a temperature controller, all contained in a single enclosure. Up to 20 LPM of clean dry air can be supplied at pressure up to 4 bars by the self contained compressor. This was mostly used to flush the photochemical chamber for removing any remaining pollutants from previous set of experiments. A partial flow dilution tunnel was used for dilution of diesel exhaust emissions with ambient air in order to complete the coagulation and condensation processes occurring during the particulate formation. When the diesel engine is operated, carbonaceous soot particles and high boiling point hydrocarbons are emitted from the tailpipe. These hydrocarbons condense on soot to form particulate matter (PM) after being diluted with preheated air inside the partial flow dilution tunnel [37]. The dilution ratio was kept constant (20:1) for all the experiments.

DESIGN AND OPTIMIZATION OF PHOTOCHEMICAL CHAMBER

Ultraviolet (UV) fluorescent tubes were chosen as light source. UV C spectrum of the sunlight is mostly absorbed in the upper atmosphere by the ozone layer and only UV A and

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UV B spectrums reach the earth surface. Out of UV A and UV B spectrums, UV A does not play any significant role in the atmospheric photochemical reaction therefore UV B lamps were chosen for the present study to exactly simulate ambient light conditions. UV B lamps deliver light in the wavelength ranging from 280-390 nm, which is naturally available at earth surface from the sunlight. The UV B lamps (Make: Philips) have a light intensity peak at a wavelength of 313 nm. UV B lamps are most efficient for photochemical chamber experiments [38]. A typical UV B lamp employed has a life of 3000 h and its length is 24 inches and it consumes 20 watts power. 10 UV B lamps on each side of photochemical chamber were used for the experiments as shown in figure 2.

The photochemical chamber has been built and is about 180 cm × 150 cm × 90 cm (L × H × W). A fluorinated ethylene propylene (FEP) film (50 μm thick) was employed on the chamber walls in order to minimize aerosol and vapour wall reactions and to allow adequate UV-B light transmission. Walls were supported by a rigid aluminum structural frame in such a way that only FEP film surfaces faced the gases and aerosols. This prevented possible interaction and loss of radicals upon contact with metallic surfaces. UV-B ($\lambda_{max}\sim$ 313 nm) lamps were placed outside both larger sides (10 on each side) of the chamber at a distance of 10 cm from the walls. The lamps were mounted on wooden frames to protect personnel from ultraviolet (UV) light exposure. The temperature and relative humidity in the chamber were monitored by a humidity measurement sensor (Make: Testo; Model: 605 H1) inserted at the outlet of photochemical chamber. The leak tests within the chamber were conducted. The absence of any kind of contamination of the chamber is very important because the contaminants such as ambient particles as well as VOCs would ruin the experiment in the photochemical chamber. Therefore the chamber was tested for particle concentrations and nucleation of particles using a CPC to ensure that the aerosol number concentrations are well below 50-100 particles per cc. Inside of the chamber, FEP membrane was cleaned once with ethanol and then twice with Milli-Q water and then the chamber was flushed with zero air for at least 2 h to remove any possible traces of contamination. The UV radiation itself can also react with impurities and is therefore used as a cleaning tool in this study. When the air was sufficiently clean (< 100 particles/ cm^3), then the engine exhaust was introduced in the chamber. The UV lamps were used to raise the temperature in the chamber to approximately 35°C.

Chamber performance was optimized for all the engine loads at a fixed engine speed (rated engine speed of 1800 rpm) in such a way that it resembled the atmospheric conditions. Temperature and RH were maintained for all the experiments in the range of 35-45°C and 40-60% respectively by adjusting the flow and by addition of zero air. Measurements were made for four different loads (0%, 20%, 40% and 60% of rated load) at a constant engine speed of 1800 rpm for optimization of photochemical chamber. Dilution ratio for each load was kept constant at 20. The engine experiments could not be carried out at higher engine loads (80 and 100% rated load) because the temperature and RH exceeded beyond limits and could not be controlled. Before every measurement, photochemical chamber was flushed out with zero air for at least 2 h. The engine was operated for more than 4 h for each load for every measurement in order to provide enough time for secondary aerosol formation. The inlet flow rate through the chamber was always kept constant to approximately 25 LPM. Volume of the photochemical chamber was 2430 L and when it was filled with diesel emission, it got bulged. Thus actual volume of inflated chamber was 2916 L hence the calculated aerosol residence time was approximately 117 minutes.

For assessing the wall losses within the photochemical chamber, experiments were carried out at 40% rated load with UV B lights turned off. Measurements were recorded upstream and downstream of the chamber for OC and EC. Based on the values of EC upstream and downstream of the chamber, average aerosol losses inside the chamber were calculated and found to be approximately 36%. The results for the subsequent set of experiments for secondary/ aged emissions were multiplied by this correction factor.

RESULTS AND DISCUSSION

Engine was operated with diesel fuel at a fixed speed of 1800 rpm (rated speed) for varying loads: 0%, 20%, 40% and 60%. All the instruments were calibrated and measurements were obtained for primary as well as secondary diesel aerosols. The main objective of this study was to look at the ratio or percentage change between the primary and secondary tailpipe emissions with focus on SOC using diesel fuel at different engine load conditions. All the engine tests and measurements were carried out three times for each data point and the average values are reported. The standard deviation was below 2%.

EFFECT OF TEMPERATURE AND RELATIVE HUMIDITY

Engine exhaust temperature increases with increasing engine load therefore the temperature of the diluted exhaust in the photochemical chamber increases with increase in engine load (Figure 3). Higher chamber temperature helps in oxidation of VOCs into SOC to a certain extent but also results in lower gas to particle conversions if the temperatures are too high. Therefore the oxidation of the VOCs becomes more efficient with increasing engine load. Gas-to-particle conversion also depends on chamber temperature. Hence higher formation of new particles takes place at relatively

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lower temperatures due to reduced vapour pressures of SVOCs [25].

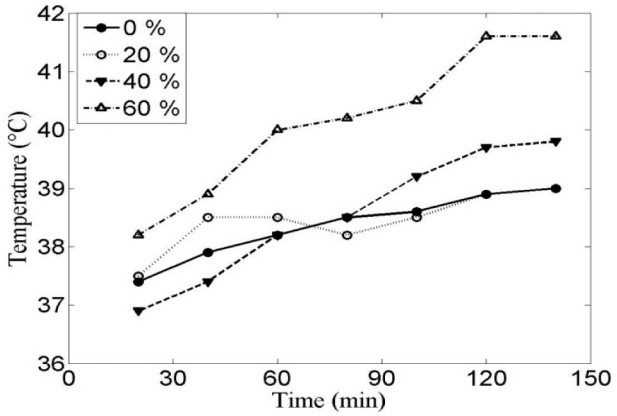

Figure 3. Temperature profile inside the photochemical chamber for different engine loads.

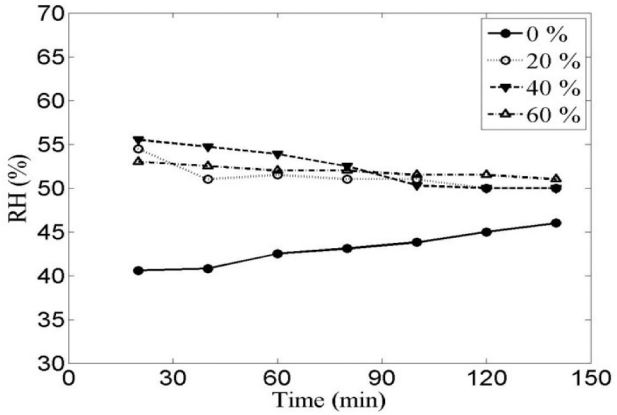

Figure 4. RH profile inside the photochemical chamber for different engine loads.

Relative humidity inside the photochemical chamber hardly increases with engine load (figure 4) except for a really low value at no load condition. Relative humidity in diesel engine emission comes due to water release which is a major combustion product. For no load condition, relative humidity is quite low in comparison to other engine loads which allow rapid ageing. Relative humidity has a different effect on condensation, adsorption and absorption of SVOCs on the pre-existing primary exhaust particles as water vapour starts competing with SVOCs for condensing on the limited particle surface area available [39]. For longer runs, humidity goes down inside the chamber possibly due to rise in photochemical chamber temperature caused by warmer diesel exhaust and heating due to UV lamps.

PRIMARY AND SECONDARY OC/ EC MEASUREMENTS

Figure 5 summarizes the information of primary emissions entering the photochemical chamber. OC and EC present in primary emissions increase with increasing engine load. Quantity of diesel injected for combustion increases with increasing engine load, whereas the quantity of air available for combustion remains same (because engine speed remains constant). Higher combustion temperatures and richer fuel air mixtures at high engine load favors lower amount of organic species formation and higher amount of elemental carbon formation due to pyrolysis of fuel.

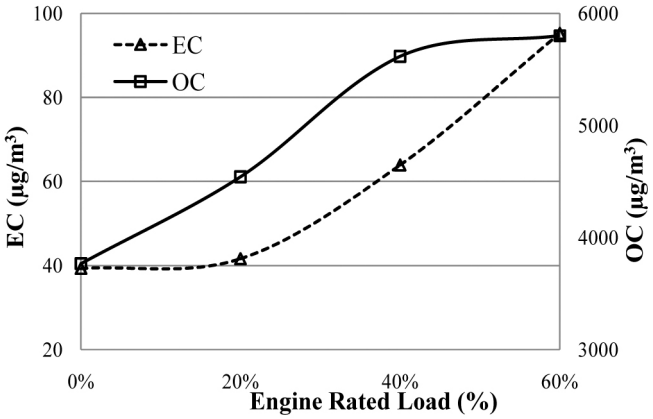

Figure 5. Trends of primary EC and OC emissions for different engine loads.

The OC/ EC measurements were also carried out for secondary aerosols aged in the photochemical chamber (Figure 6, 7).

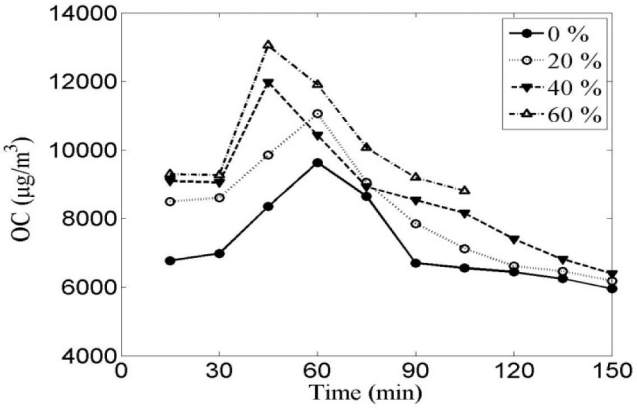

Figure 6. OC measurements in aged aerosol for different engine loads with time.

Peaks for OC in secondary organic aerosols at higher engine loads (60% and 40%) is reached earlier because of higher primary particle concentration in the photochemical chamber, which provides extra surface area for condensation and

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subsequent ageing. Whereas at lower engine loads (0% and 20%), OC peaks get delayed because of relatively lower primary particles available inside the photochemical chamber. Earlier studies have also reported that absorption and adsorption phenomenon is dominant over the homogeneous condensation of SVOCs inside the photochemical chamber [25]. Here homogenous condensation of VOCs might be the dominant mechanism for particle formation. After ageing, particles that have grown into bigger particles settle down within the chamber due to gravitational forces and hence lesser OC is found. Since, the chamber residence time was 117 min and the measurements for secondary aerosol were for only 150 min, only one cycle could be observed. It is expected, as shown by previous studies on photochemical chambers, that such cycles are repetitive with the peaks reducing in the subsequent cycles and the chamber attaining some sort of steady state concentrations [40]. The peaks really show the fresh set of nucleated, condensed, and grown aerosols, which keep on growing as they pass out through the chamber and in the process they might get lost due to coagulation, impaction, and gravitational settling. Figure 7 shows variation of EC concentration with respect to engine load in the secondary aerosols.

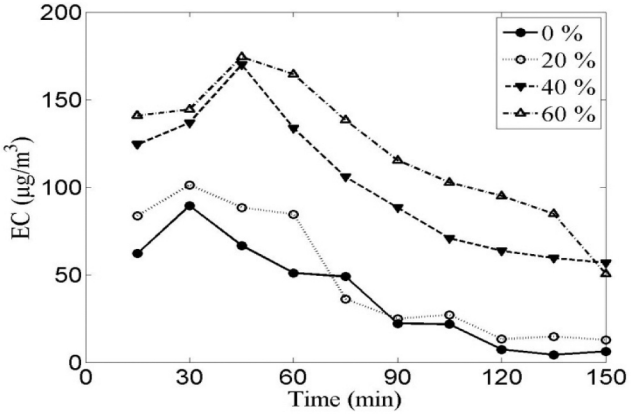

Figure 7. EC measurements in aged aerosol for different engine loads with time.

At higher engine loads, combustion occurs at relatively higher temperature and hence fuel is burnt more efficiently. Higher combustion temperatures results in emission of more elemental carbon compared to that of lower engine loads. At higher engine loads, elevated EC concentration can be seen due to relatively higher combustion of lubricating oil [19]. In the process of ageing in photochemical chamber, EC provides the crucial nuclei surface on which organic carbon deposits and grows further. Hence, excess of soot/ EC automatically leads to higher number concentration of secondary aerosols. Ageing process doesn't affect the concentration of EC. EC concentration after long time in chamber goes below primary value because of particle loss due to gravitational settling in the chamber.

YIELD OF SOC FOR DIFFERENT ENGINE LOAD CONDITIONS

At lower engine loads, very little fuel in injected and combusted in excess air leading to relatively lower combustion chamber temperatures. This results in unburned hydrocarbons emissions and cold combustion product formation. Whereas at higher engine loads, air-fuel ratio comes closer to stoichiometric ratio and combustion takes place at relatively higher temperatures. The SOC yield can be expressed as the ratio of OC_{aged}/ $OC_{primary}$ (Figure 8). Another novel idea of looking at the SOC yield could be in terms of the ratio of OC_{aged}/ $EC_{primary}$ (Figure 9).

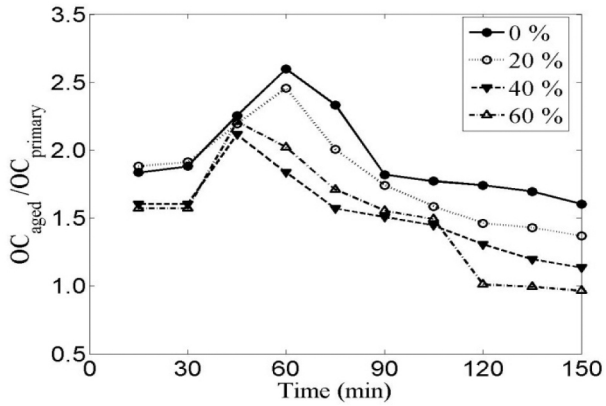

Figure 8. OC_{aged}/ $OC_{primary}$ for different engine loads with time.

Ageing at 0% load is highest because of excess unburned fuel and lubricating oil appearing as gaseous hydrocarbon emissions that eventually condense into particulate phase inside the photochemical chamber. In addition, at this load relative humidity is quite low (Figure 4) which allows more ageing on particles because of adsorption, absorption and condensation of SVOCs on particles.

Figure 9 shows aged OC emission with time for different load conditions normalized with respect to elemental carbon produced at each load. Here it can be seen that if the emissions are normalized with respect to EC, then the maximum SOCs are formed for 20% engine load condition. This needs to be investigated further.

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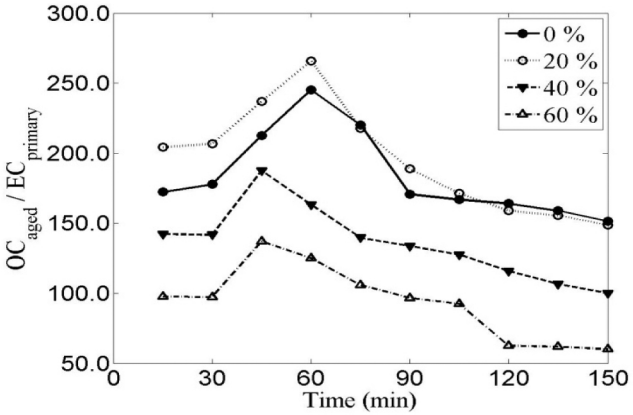

Figure 9. $OC_{aged}/EC_{primary}$ for different engine loads with time.

PRIMARY AND SECONDARY PARTICIPATE BOUND PAHs MEASUREMENT

The primary PAH emissions from the diesel particle exhaust for various engine load conditions are shown in figure 10. It can be seen that the particle bound PAH emissions increase steadily with increasing engine load therefore suggesting their higher toxic potential.

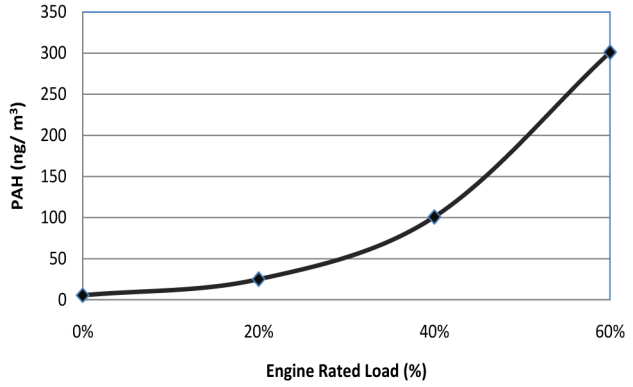

Figure 10. Primary PAH emissions for different engine loads.

Figure 11 provides the time resolved particle bound PAHs present on secondary aerosols coming out of the photochemical chamber for varying engine load conditions.

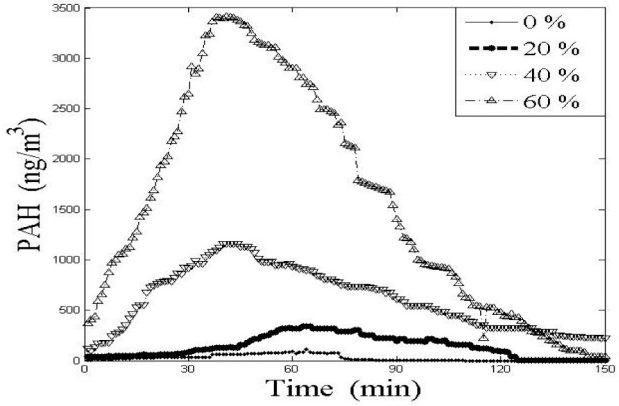

Figure 11. Total particle bound PAH on aged aerosols for different engine loads.

It can be observed from figure 11 that peaks for ageing of PAHs appear earlier for higher engine loads (60% and 40%) whereas they appear relatively later for lower engine loads (0% and 20% loads). Peaks of ageing for PAHs appear earlier for 40% and 60 % loads and are delayed at lower loads. At 60% load, there is a large amount of PAHs formation observed and that needs to be further investigated.

This instrument was factory calibrated with known PAH standards. Toxicity of the individual PAH species can be an order of magnitude different from each other. In the present study, speciation of PAHs has not been carried out therefore it gives merely a bulk idea of 'Toxicity'.

PARTICLE NUMBER CONCENTRATION MEASUREMENTS

Figure 12 shows the time resolved particle number concentration for secondary aerosols sampled from the photochemical chamber for different engine load conditions.

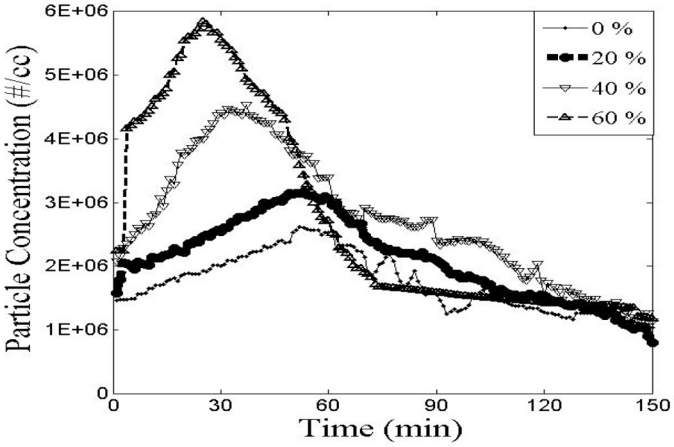

Figure 12. Particle concentration (#/cc) in aged aerosol for different engine loads with time.

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Particle number concentration increases as engine load increases. For higher engine loads (60% and 40%), ageing becomes faster due to dominance of nucleation of particles therefore the peak of number concentration appears earlier. This number concentration goes down quickly because of agglomeration of smaller particles into bigger particles. At lower engine loads (0% and 20%), ageing process is primarily due to absorption, adsorption of SVOCs on pre-existing particle therefore secondary particle formation process is slower. This is the reason, why the number concentration peaks are seen relatively later and not so prominent.

COMPARISON OF AGED AEROSOLS FOR DIFFERENT ENGINE LOADS

Table 2 provides a summary of the secondary emissions sampled at the outlet of the photochemical chamber for different engine load conditions. Only the peak values are presented here in order to compare the SOC yields at different engine load conditions. These values are important because they represent the maximum toxic potential of the secondary aerosols originating from a diesel fuelled CRDI engine.

Table 2. Comparison of peak EC, OC and PAH values in aged aerosol for different engine loads.

	0%	20%	40%	60%
EC (µg/m^3)	89	101	169	174
OC (µg/m^3)	9634	11060	11973	13046
PAH (ng/m^3)	115	342	1163	3414

As discussed previously, the maximum absolute SOC forms at 60% load. However, the relative amount of SOC when normalized with primary OC and EC are highest for 0% and 20% loads respectively. Another important observation is made regarding the particle bound PAHs, which increase by an order of magnitude after ageing (as seen from figure 10 and table 2), which indicates that the toxic potential of diesel engine exhaust increases an order of magnitude even under moderate ageing conditions.

CONCLUSIONS

CRDI engine emissions have been moderately aged under simulated ambient conditions using a newly developed photochemical chamber. From the experimental data and analysis thereof, several key observations have been made. Exhaust emission ageing was carried out within the temperature range of 35- 45°C and RH range of 40-60%. Primary emissions of OC, EC and PAHs increased in diesel exhaust with increasing engine load. With increase in engine load, rate of primary EC emission is higher than rate of increase of OC emissions. At lower engine loads, due to relatively lower RH (~40%), the process of ageing is accelerated and deposition of SVOCs on pre-existing primary particles (EC) takes place resulting in bigger secondary particles. At higher engine loads, EC nuclei concentrations are higher, which lead to quicker heterogeneous condensation of OC on these large nucleation sites therefore overall number concentrations of secondary particles increase. At higher engine loads, ageing takes place primarily due to particle agglomeration. Coagulation is the dominant mechanism here although nucleation, condensation, adsorption and oxidation, all happen inside the photochemical chamber. The maximum absolute secondary OC forms at 60% engine load, which is the highest loading of the engine for this investigation. However, the relative amount of SOC when normalized with primary OC and EC are highest for 0% and 20% loads respectively. Another important observation is made regarding the particle bound PAHs, which increase by an order of magnitude after ageing, which indicates that the toxic potential of diesel engine exhaust might increase an order of magnitude even under moderate ageing conditions.

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