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Impact of a diesel car on primary and secondary organic aerosols

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Photo-oxidation experiments where performed at different dilution factors in a smog chamber filled with exhaust produced by a EURO 3 diesel car at idling mode. At high dilution, fresh aerosols consist mainly of black carbon (BC) with a low fraction of organic matter while a typical photo-oxidation experiment shows a substantial increase of organic aerosol. In fact, UV-initiated oxidation of diesel exhaust rapidly produces large amounts of SOA which leads to an increased OM/BC ratio. There might be a future need to introduce the SOA production potential for traffic emission regulation purposes.

1. Introduction

At present, primary organic aerosol (POA) emissions from sources such as vehicles are treated as non-volatile in air quality models. Recent findings have shown that the particulate matter with a diameter lower than 2.5 µm (PM2.5) emitted by diesel power generator can decrease by 50% when the dilution ratio is increased from 20:1 to 350:1 (Lipsky and Robinson, 2006). This decrease is because POA contains semi-volatile organic compounds (SVOCs) that partially evaporate. In the atmosphere these compounds are then involved in different photochemical reactions and the products generated from the photochemistry have a lower volatility than the parent compounds hence they nucleate creating new particles or they undergo adsorption onto pre-existing aerosol surfaces and/or absorption into the aerosol organic matter. These processes can be the reason for the unexplained secondary organic aerosol (SOA) production (Robinson et al., 2007). In fact, the oxidation of traditional SOA precursors such as light aromatics from diesel exhaust can explain only a small fraction of the SOA formed from the photo-oxidation of diesel exhaust during smog chamber experiments (Weitkamp et al., 2007). SOA can be a major contributor to fine particulate levels in both urban and rural atmospheres (Lanz et al., 2007; Turpin and Huntzicker, 1995). In order to better understand the contribution of diesel exhaust to ambient POA and SOA, photo-oxidation experiments were performed at different dilution factors, some of them atmospherically relevant, in a smog chamber filled with exhaust produced by a EURO 3 diesel car at idling mode. The temporal evolution of the organic carbon to black carbon ratio from fresh diesel emissions is reported here.

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2. Materials and method

2.1 Experimental setup

The experiments were carried out in the Paul Scherrer Institut (PSI) smog chamber. The 27-m^3 bag is temperature controlled and four xenon arc light sources are used to simulate the atmospheric light spectrum (Paulsen, et al., 2005). Diesel exahast was introduced into the chamber from a real diesel car running in idling mode. The injection took place after the engine had reached its normal operating temperature.

The exhaust was diluted with zero air with an ejector diluter (Dekati diluter) with a dilution factor of about 10 to avoid coagulation. The transport line, the ejector diluter and the dilution air where heated to 150 °C in order to avoid condensation of semivolatile organic compounds. The CO_2 concentrations in the exhaust was measured before the ejector diluter and in the smog chamber to calculate the exhaust dilution ratio.

The high concentration of NO from diesel engines (HEI, 2002) slows the photochemistry down considerably. Therefore, propene and ozone were added to the exhaust in the chamber during the experiments to make the photochemistry faster. Ozone was added to reduce the NO concentration and propene was added to increase the VOC/NO_x ratio.

2.2 Instruments

A high-resolution time-of-flight aerosol mass spectrometer (HR-ToF-AMS) and a quadrupole aerosol mass spectrometer (Q-AMS) were used for the experiments to quantify the organic aerosol. The AMS provides an averaged mass spectrum and the size-resolved chemical characterization of non-refractory components of an ensemble of particles in real time. A detailed description of the two instruments is reported elsewhere (Jayne et al., 2000; DeCarlo et al., 2006).

To quantify the black carbon (BC) concentration an aethalometer was used which collects the aerosol on a filter and simultaneously measures the absorption of light through this filter at various wavelengths. The instrument configuration minimizes the influence of scattering which can affect the BC measurements. The data were corrected for scattering artefacts in the filter using the procedure by Weingartner et al. (2003). The corrected absorption coefficients were then converted to BC concentrations using a mass absorption efficiency of 7.76 m^2/g.

3. Results

A preliminary analysis of these experiments shows a decrease of the OC/BC ratio with increasing dilution ratio as expected from the studies cited above. The low values (~ 0.2) found at high dilution factors (500-1000) indicate that under these conditions for a diesel car at idle mode, fresh aerosols consist mainly of BC with a low fraction of organic matter. The OC was obtained by assuming a collection efficiency of 1 for the AMS data and dividing the measured organic matter (OM) mass by a factor of 1.2, a characteristic OM/OC value for non-oxidized organics from vehicles emissions. These preliminary results need to be confirmed with more experiments.

The decrease in the POA loading with increasing dilution is due to repartitioning of SVOCs to the gas phase due to dilution (Robinson et al., 2007). However, the photo-oxidation of SVOCs leads to the production of less volatile compounds which condense, forming SOA. The increase of the organic aerosol mass loading with time due to the photo-oxidation for a typical experiment is shown in Figure 1. The initial organic concentration, corresponding to the POA, was ~2 μg/m^3. At time zero, the lights were turned on and the photochemistry started producing SOA. After 3 hours the organic matter measured was ~11 μg/m^3. The data are not corrected for wall-losses.

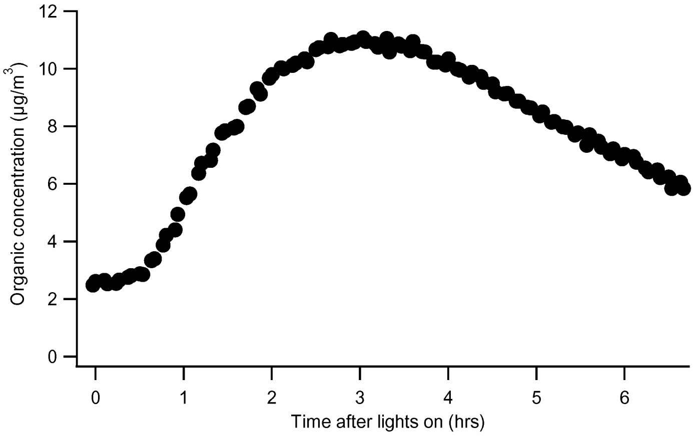

Figure 1. Time series of particulate organic mass during a smog chamber experiment

In Figure 2 the temporal evolution of the ratio of organic mass to black carbon mass (OM/BC) for a diesel exhaust aging experiment is presented. The ratio increases by nearly a factor of 4 until a constant value around 1.4 is reached.

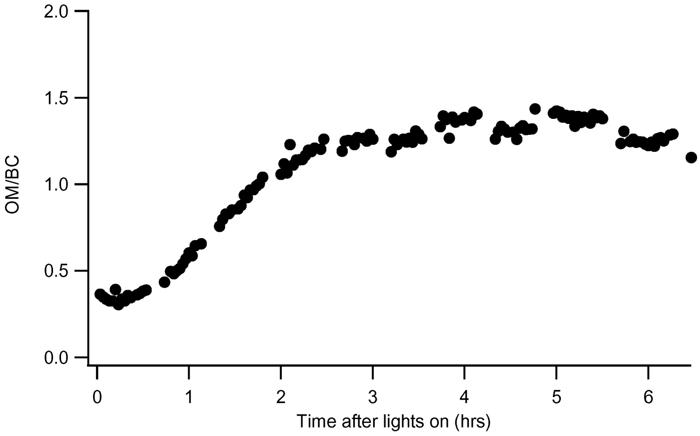

Figure 2. OM/BC time series during a smog chamber experiment

4. Conclusions

Smog chamber aging experiments have demonstrated that fresh aerosols from a diesel car consist mainly of BC with a low fraction of organic matter at high dilution ratios. Photo-oxidation of diesel exhaust rapidly produces SOA which leads to an increased OM/BC ratio. The determination of the actual ratio of SOA/POA under atmospheric conditions is subject of further analysis.

The introduction of aftertreatment devices such as catalytic converters and particle traps and the optimization of the engine combustion process have lowered diesel primary emissions significantly for newer diesel cars however, the possibility of considerable SOA production from diesel emissions in the atmosphere has not been taken into consideration by legislation.

This SOA formation might also be relevant from a health perspective. In some cases the products of the photo-oxidation of organic compounds in the atmosphere are more toxic than the parent compounds because they do not require metabolic activation in order to exert genotoxicity, including mutagenicity and tumorigenicity (Yu, 2002). Consequently, there might be a future need to introduce the SOA production potential for traffic emission regulation purposes.

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