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Megacity pollution by modern Diesel cars: New insights into the nature and formation of volatile nano-particles with high lung intrusion efficiency

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Aerosol particles generated by Diesel vehicles represent mayor health affecting air pollutants in cities and near motor ways. To mitigate the Diesel particle pollution problem, Diesel vehicles become increasingly fitted or retro-fitted with modern exhaust after treatment systems (ATS), which remove most engine-generated primary particles, particularly soot. Unfortunately however, ATS have undesired side effects including also the formation of low vapour pressure gases, which may undergo nucleation and condensation leading to volatile nucleation particles (NUP). NUP are substantially smaller (diameters: 5-15 nm) than soot particles (diameters: 40-100 nm), and therefore may be termed real nano-particles. NUP can intrude with maximum efficiency the lowest, least protected, and most vulnerable compartment of the human lung. However, the chemical nature and mechanism of formation of NUP are only poorly explored.

Using a novel mass spectrometric method, we have made the first on line and off line measurements of low vapour pressure NUP precursor gases in the exhaust of a modern heavy duty Diesel vehicle engine, operated with and without ATS and combusting low and ultra-low sulphur fuels including also bio fuel. In addition, we have made accompanying NUP measurements and NUP model simulations.

The on line measurements involved a CIMS (Chemical Ionization Mass Spectrometry) method originally developed by MPIK. They took place directly in the Diesel exhaust and had a large sensitivity and a fast time response (1 s). The off line measurements involved adsorption of exhaust gases on stainless steel, followed by thermo desorption and detection of desorbed exhaust molecules by CIMS.

We find that modern Diesel ATS strongly increase the formation of hydroxyl radicals, which induce conversion of fuel sulphur to the important NUP precursor gaseous sulphuric acid. We also find that appreciable amounts of di-carboxylic acids survive the passage of the ATS or are even formed by the ATS. Our measurements indicate that gaseous sulphuric acid drives new NUP formation by nucleation and that gaseous di-carboxylic acids have an important role in NUP growth by condensation. Since the ATS increases OH and NO2 formation, it may also promote the formation of highly carcinogenic hydroxyl and nitro groups containing polycylic aromatic hydrocarbons. If so, these will also condense on NUP. Hence, NUP may serve as very efficient carriers transporting carcinogenic species into the deepest compartment of the human lung. Due to their small mass, NUP are not considered by present air quality regulations, which are particle mass, rather than particle number and particle surface oriented. Considering their high lung intrusion efficiency, large number, and large surface, NUP deserve increased future attention.