In-situ Characterisation of the Composition and Surface Functionalities of Black Carbon Containing Particles

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Black carbon (BC) containing emissions from diesel engines and solid fuel combustion have well documented but poorly constrained effects on human health and global climate (Bond et al., 2013). Our ability to describe and quantify these effects are hindered by limited knowledge of the detailed physico-chemical properties of BC-containing aerosol and the links between these properties and the effects on health and climate.

The aim of this work was to investigate the composition of BC-containing emissions using the Soot particle aerosol mass spectrometer (SP-AMS; Onasch et al. 2012) and novel in-situ surface analysis using X-Ray Photoelectron Spectroscopy (XPS).

Model soot particles were produced using atomization of a carbon black material (Regal Black) and the CAST soot generator. Real world BC-containing emissions were investigated from a conventional wood stove and a EURO II diesel engine. Atmospheric aging was carried out using flow tubes and a Teflon smog chamber. The SP-AMS was used in the dual vaporizer configuration. The tungsten vaporizer (600 C), which vaporizes non-refractory components only, was supplemented in intervals with IR laser vaporization (continuous wave Nd-YAG laser; 1064 nm) to investigate refractory components.

With the XPS technique, the surface chemical composition of fresh and aged soot particles were investigated. Particles from the CAST generator were focused into vacuum using an aerodynamic lens inlet. The particle beam was overlapped with a 360 eV synchrotron light beam at Max-Lab (Lund University) and the emitted photoelectron energies were analyzed.

Measurements on black carbon particles from the investigated systems could be divided into a number of classes of fragments, based on their composition and volatility. Non-refractory molecular fragments detected with flash vaporization were dominated by hydrocarbon clusters from hydrocarbons for diesel exhaust. For biomass combustion a complex mixture of hydrocarbons and oxidized fragments were found (including anhydrous sugars and phenols). For diesel exhaust only a minor fraction of the particle mass was detected with flash vaporization at 600 °C.

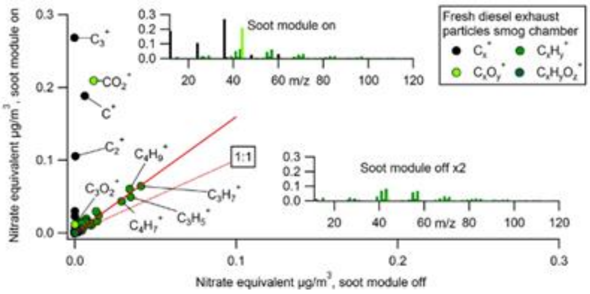

Figure 1: Mass spectra of fresh diesel exhaust particles. Scatterplot data recorded with soot module on versus off. Hydrocarbon ion intensities increase uniformly. Carbon clusters and carbon and oxygen containing ions increase by highly variable factors, indicating refractory components.

When the soot module (laser vaporizer) was engaged, ions due to refractory components were added to the mass spectra. These include pure carbon clusters (predominantly C1-C5) as well as significant amounts of carbon and oxygen containing ions for all investigated soot sources. We hypothesize that the latter represent partial oxidation of the soot core, which occurred during soot formation. We found weaker increases in small hydrocarbon fragments, indicative of hydrogen bound to the core in less matured soot. A number of metals were identified with high time resolution, for example Zinc in biomass combustion.

Preliminary analysis of the surface specific analysis with in-situ XPS on the carbon edge, showed a shift towards higher binding energies for BC particles exposed to ozone, suggesting an increase in oxygenated organic species at the soot particle's surface.

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Bond, TC., et al. JGR-A 118.11 (2013): 5380-5552.
Onasch T. et al. AS&T 46, 804-817, (2012)