Organic functional group composition of particulate matter from fresh and aged biomass burning and coal combustion emissions

*Amir Yazdani[1], Nikunj Dudani[1], Satoshi Takahama[1], Amelie Bertrand[2], André S. H. Prévôt[2], Imad El Haddad[2], Ann M. Dillner[3]

1. ENAC/IIE Swiss Federal Institute of Technology Lausanne (EPFL), Lausanne, Switzerland, 2. Laboratory of Atmospheric Chemistry, Paul Scherrer Institute, Villigen, Switzerland, 3. Air Quality Research Center, University of California Davis, Davis, California, USA

Particulate matter (PM) affects visibility and climate through light scattering, direct and indirect radiative forcing, and purturbing cloud formation. In addition, exposure to fine PM is known to cause adverse health effects and increase mortality. Organic matter (OM), can make up more than half of the total fine atmospheric PM, and yet its composition and formation mechanisms are not fully characterized due to its complex chemical composition. Biomass burning (e.g., residential wood burning, wildfires, and prescribed burning) and coal combustion (for heat and power generation) are two major OM sources, for which the impact of atmospheric aging - including secondary organic aerosol (SOA) formation - is not yet fully clear.

In this study, we investigated the effect of aging on composition and mass concentration of organic aerosols of wood burning (WB) and coal combustion (CC) emissions using mid-infrared spectroscopy and aerosol mass spectrometry (AMS). For this purpose, primary burning aerosols were injected into the Paul Scherrer Institute (PSI) environmental chamber and aged using hydroxyl and nitrate radicals to simulate day-time and night-time oxidation processes in the atmosphere. In these experiments, aerosols reached an oxidative age comparable to that of atmospheric aerosols. A time-of-flight AMS was used to measure the high-time-resolution composition of non-refractory fine PM, while we collected PM_1 aerosols on PTFE filters before and after four hours of aging for off-line Fourier transform-infrared spectroscopy (FT-IR) measurements.

AMS and FT-IR estimates of organic aerosol mass concentration were highly correlated ($r^2=0.92$), both indicating an approximately three-fold increase in organic aerosol concentration after aging. The OM/OC ratio, indicating the extent of oxidation, also agreed closely between the two instruments and increased, on average, from 1.6 (before aging) to 2 (after aging). Mid-infrared spectroscopy, which is able to differentiate among oxygenated species, shows distinct functional group compositions for aged WB aerosols (high abundance of carboxylic acids) and CC aerosols (high abundance of non-acid carbonyls) and detects considerable amounts polycyclic aromatic hydrocarbons (PAHs) for both sources.
Mid-infrared spectra of fresh WB and CC aerosols are reminiscent of their parent compounds with differences in specific functional groups, showing the dominant oxidation pathways for each emission source. Finally, the comparison of mid-infrared spectra of aged WB aerosols in the environmental chamber with that of ambient samples affected by residential wood burning and wildfires, reveals interesting similarities regarding the high abundance of alcohol COH and the visible signatures of lignin. This finding is useful for interpreting sources of atmospheric aerosols and better understanding their complex mid-infrared spectra.

Keywords: Mid-infrared spectroscopy, Biomass burning , Organic aerosol, AMS, Environmental chamber, FTIR

