

Day-night differences in the composition and sources of carbonaceous aerosol at a polluted regional background site in the Netherlands

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The origin of carbonaceous aerosol differs during day- and night-time, because emissions from major sources such as traffic, biomass combustion, and secondary organic aerosol formation show a distinct diurnal pattern. Moreover, photochemical processing and evaporation of semi-volatile organic compounds are enhanced during day-time, due to the availability of sunlight and higher temperatures. Assessing day-night differences in sources and chemical composition can give an indication of the importance of local/regional carbon sources and processing, since day-night differences should be averaged out during long-range transport. If local sources dominate, one could expect a strong diurnal variation in the source profile, but if long-range transport dominates the diurnal variation would be much weaker.

In this study we measure the isotopic (^{14}C and ^{13}C) and detailed chemical composition of the organic fraction of the aerosol on high volume PM_{2.5} filter samples that were collected separately during day and night time. Radiocarbon (^{14}C) measurements are used to estimate three main aerosol sources of organic and elemental carbon (OC and EC): Fossil fuel combustion (ff), biomass combustion (bb), and biogenic sources (bio). The detailed chemical and stable isotopic composition are measured at different desorption temperatures from the filter, which separates the more and less refractory organic compounds. The composition of the organic aerosol is measured using an thermal-desorption Proton Transfer Reaction Time-of-Flight Mass Spectrometer (PTR-ToF-MS) method (Holzinger et al, 2010) and the stable isotopic composition is measured using a thermal desorption IRMS method (Dusek et al., 2013).

Source apportionment results using ^{14}C show that the contribution of fossil fuel combustion to EC and OC is higher during day-time than during night-time. This is valid for all seasons. During night-time biomass combustion plays a bigger role as a source of carbonaceous aerosol. Even in the summer, when biomass combustion is a small source, its relative contribution increases between 19:00 and 07:00. However, the diurnal changes in source contributions are relatively moderate (e.g., the biomass burning contribution to TC increased from 31% to 43% for the winter sample with the most distinct day-night difference.) This highlights the importance of long-range transport as a source of the carbonaceous aerosol in this region.

First results from chemical composition measurements on four of the samples show that the concentration of less refractory organic carbon (desorption temperature up to 200 °C) increases at night-time much more strongly than the concentration of the more refractory carbon. Similarly, the concentration of small organic compounds with $m/z < 100$ also increases more strongly than heavier compounds. This indicates partitioning of semi-volatile OC as a possible additional night-time source. The chemical composition will be studied in more detail, focusing on diurnal changes in O/C ratios, individual compounds and compound classes, such as hydrocarbons or organic acids.

Dusek, U., Meusinger, C., Oyama, B., Ramon, W., de Wilde, P., Holzinger, R., and Röckmann, T.: A thermal desorption system for measuring $\delta^{13}\text{C}$ ratios on organic aerosol, *Journal of aerosol science*, 66, 72-82, 2013.

Holzinger, R., Williams, J., Herrmann, F., Lelieveld, J., Donahue, N., Röckmann, T., 2010. Aerosol analysis using a Thermal-Desorption Proton-Transfer-Reaction Mass Spectrometer (TD-PTR-MS): a new approach to study processing of organic aerosols. *Atmospheric chemistry and physics* 10, 2257-2267.