Characterization of carbonaceous aerosol in Emilia-Romagna in the Supersito Project: Influences of the Thermal-Optical measurement protocols

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The carbonaceous component of atmospheric aerosols was characterized in two intensive monitoring campaigns conducted in the Emilia Romagna region (Northern Italy) in cold seasons through the years 2011, 2012 and 2013, in the framework of the Supersito project. The $PM_{2.5}$ samples were collected in four monitoring stations describing different emission situations in the region: the main city Bologna (MS), two urban sites in smaller cities (Parma and Rimini) and one rural background (SP).

This study investigated the thermal-optical transmittance method (TOT), with specific concern to the open debate on discrimination between organic and elementary carbon (OC/EC) in heavily loaded filters.

Using the EUSAAR2 protocol (Cavalli *et al.*, 2010), quality assurance procedures showed good linearity up to OC concentration of 160 µg cm^{-2}, quantification limits as low as 1.5 µg cm^{-2} and 9.0 µg cm^{-2} for EC and OC, respectively, and an excellent reproducibility (relative Standard Deviation ≈ 5% after 7 months). In addition, the reliability of the measurement of total carbon content has been proved by the good agreement with the results obtained using a CHNSO elemental analyzer (relative difference lower than 6%).

Using the conventional sampling procedure (flow rate of 2.3 m^3 h^{-1} to collect 55 m^3 day^{-1}), several samples collected at MS and SP sites in 2011-2012 winter showed filter blackening, likely ascribed to high concentrations of light-absorbing carbonaceous aerosol (higher than 15µg cm^{-2} on the filter corresponding to 7.5µg m^{-3} of EC in the air). This makes it difficult for the laser to register any changes in transmission so limiting changes of an unbiased correction of the pyrolytic carbon contribution. The consequence is that negatively biased EC values were obtained for these PM filters (Piazzalunga, *et al.*, 2011).

In order to explain such drawbacks, the chemical composition of the sampled material has been investigated, with specific concern to organic compounds produced by biomass combustion. These substances have been found to strongly affect light absorption and charring behavior of the PM filters. For this reason, the contribution of both open and residential biomass combustion was investigated, by evaluating the concentration of selected polycyclic aromatic hydrocarbons (PAHs), as relevant markers of biomass combustion processes. In particular, the monthly average concentrations of the following PAHs were studied in the investigated sites: pyrene, fluoranthene, benzo[a]anthracene, chrysene, benzo[b]fluoranthene, benzo[j]fluoranthene, benzo[k]fluoranthene and benzo[a]pyrene. In the investigated period, higher PAH concentrations of ≈ 6-7 ng m^{-3} were found at MS and SP in comparison with the other sites (≈ 4.3 ng m^{-3} at Parma and Rimini), indicating a larger contribution of emissions from residential wood burning. This result is also confirmed by the abundance of levoglucosan, as unambiguous tracer for biomass burning emissions. (≈1000 ng m^{-3} in late fall 2011) (Pietrogrande, *et al.*, 2014).

To reduce the loading of light-absorbing carbonaceous aerosol on the filter, the sampling protocol has been changed by lowering the collected air volume to 24 m^3 per day: such limited filter loadings provide an unbiased OC/EC discrimination for all the analyzed PM samples.

In winter 2011-2012 TC mean values ranged from 9.5 µgm^{-3} in San Pietro to 12 µgm^{-3} in Parma, EC from 1.9 µgm^{-3} in Parma to 2.3 µgm^{-3} in Rimini, OC from 8.5 at San Pietro to 10.7 µgm^{-3} in Rimini. In winter 2012-2013, lower values were obtained, with TC values ranging from 7.8 to 9.1 µgm^{-3} consisting of OC from 6.3 to 6.9 µgm^{-3} and EC from 1.2 to 2.2 µgm^{-3}. In general, the obtained values were similar to the data found in several studies carried out in Northern Italy in cold periods (Sandrini, *et al.*, 2014).

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