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INTER-COMPARISON OF CARBON CONTENT IN PM_{10} AND $PM_{2.5}$ MEASURED WITH TWO THERMO-OPTICAL PROTOCOLS IN A MEDITERRANEAN SITE

E. Merico[1], D. Cesari[1,2], A. Dinoi[1], A. Gambaro[2,3], E. Barbaro[2,3], M.R. Guascito[1,4], L.C. Giannossa[5], A. Mangone[5], D. Contini[1]

[1]*Istituto di Scienze dell'Atmosfera e del Clima, ISAC-CNR, Lecce, Italy*
[2]*Istituto per la Dinamica dei Processi Ambientali, IDPA-CNR, Venezia-Mestre, Italy*
[3]*Dipartimento di Scienze Ambientali, Informatica e Statistica, DAIS, Università Ca' Foscari di Venezia, Venezia-Mestre, Italy*
[4]*Dipartimento di Scienze e Tecnologie Biologiche e Ambientali, DiSTeBA, Università del Salento, Lecce, Italy*
[5]*Dipartimento di Chimica, Università degli Studi di Bari Aldo Moro, Bari, Italy*

Carbonaceous fraction of atmospheric particulate matter (PM), generally ranging between 20% and 50% of PM mass [1], is usually classified into organic carbon (OC), elemental carbon (EC) and inorganic carbon (IC). The refractory light-absorbing component is called EC when measured by thermo-optical methods or equivalent black carbon (eBC) when measured with optical techniques. Quantification and characterization of carbonaceous particles are important to understand aerosol sources and their impact on air quality, human health, cultural heritage and climate. In fact, the European Directive 2008/50/EC requires the measurement of EC and OC in the $PM_{2.5}$ fraction of ambient PM in background areas.
A common widely used method is the thermo-optical transmittance (TOT), based on the differentiation between EC/OC according to their thermal and optical properties, using different protocols. Although a variety of inter-comparison studies of these standard approaches have been performed, the distinction between EC and OC is still a challenging problem [2], especially to maximize the comparability of results obtained in different sites. In addition, comparability of optically determined eBC and thermo-optically determined EC is also challenging because eBC and EC could vary by up to a factor 2 not only for the effect of thermal treatment but also for variability induced by size distribution, mixing state, and chemical composition [3,4,5].
In this work, a long-term campaign (January 2015-July 2016), was performed at the Environmental-Climate Observatory of Lecce (SE Italy, 40°20'8"N-18°07'28"E, 37 m a.s.l.), regional station of the Global Atmosphere Watch program (GAW-WMO) classified as an urban background site [6]. 369 daily PM_{10} and $PM_{2.5}$ samples were collected on quartz fibre filters (Whatmann, 47 mm in diameter, pre-fired for 2h at 700°C) using an automatic sampler (SWAM 5A Dual Channel Monitor, FAI Instruments srl). Simultaneous equivalent black carbon (eBC) concentrations, only for the PM_{10} fraction, were measured using a Multi Angle Absorption Photometer (MAAP Thermo Scientific, mod. 5012) operating at a wavelength of λ=670 nm using a constant mass absorption coefficient (MAC=6.6 m^2/g). Punches of 1.0 cm^2 were analysed for OC and EC determinations using a TOT method by a Sunset laboratory

O3 EAC3

carbon analyser (Sunset Laboratory Inc., OR, USA) with two different standard thermal protocols (NIOSH870 and EUSAAR2).
In summary, uncertainty of ~5% for TC and OC, compatible with the instrument manufacturer uncertainties, and larger uncertainty (~10%) for EC for both thermal protocols were found. Not statistically significant differences were found between the two protocols, for both size fractions, in TC and OC determinations. Contrarily, EC results obtained with EUSAAR2 were higher than that obtained with NIOSH870, with a difference of 19% and 33% for PM_{10} and $PM_{2.5}$, respectively. These values have a clear seasonal variability due to different combustion sources acting during cold (autumn and winter) seasons (road traffic and biomass burning). EC/TC ratios were larger for EUSAAR2 in both size fractions (23% for PM_{10} and 32% for $PM_{2.5}$), especially in the warm period (spring and summer). Differently, on average, OC/EC ratio derived from NIOSH870 was larger than obtained by EUSAAR2, being dependent on the medium-low temperature protocol.
SOC (Secondary Organic Carbon), estimated by EC-tracer method, has larger values during cold seasons, without differences between the two protocols used. The contribution of SOC to TC is essentially the same with both protocols and fractions, while SOC/OC is equal to about 51% (Figure 1) with no seasonality. Good correlation ($0.83<R^2<0.88$) was found between eBC and EC in PM_{10} even if eBC daily mean values were larger than EC measured with both protocols, as shown by the eBC/EC mean ratio, 1.62 for EUSAAR2 and 1.92 for NIOSH870 (Figure 1). The same trend was observed for both cold and warm periods.

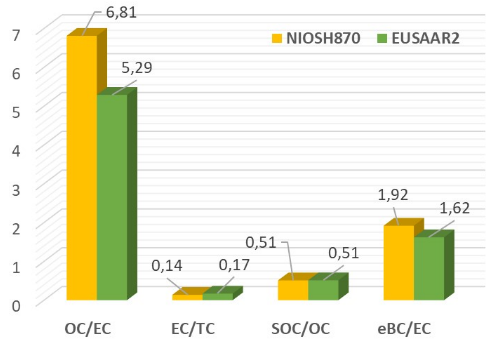

Figure 1. Comparison of some average parameters obtained with NIOSH870 and EUSAAR2 protocols.

References

[1] Putaud J.P., Van Dingenen R., Alastuey A., Bauer H., et al., Atmos. Environ., 2010, 44, 1308–1320.
[2] Brown R.J.C., Beccaceci S., Butterfield D.M., Quincey P.G., et al., Impacts, 2017, 19, 1249–1259.
[3] Hitzenberger R., Petzold A., Bauer H., Ctyroky P., et al., Environ. Sci. Technol., 2006, 40, 6377–6383.
[4] Snyder D.C., Schauer J.J. Aerosol Sci. Technol., 2007, 41, 463–474.
[5] Ram K., Sarin M.M., Tripathi S.N. Atmos. Res., 2010, 97, 335–342.
[6] Cesari D., De Benedetto G.E., Bonasoni P., Busetto M., et al., Sci. Total Environ., 2018, 612, 202–213.