Radiocarbon analysis on organic and elemental carbon in aerosol samples and source apportionment at an urban site in Northern Italy.

V. Bernardoni[1], G. Calzolai[2], M. Chiari[2], M. Fedi[2], F. Lucarelli[2], S. Nava[2], A. Piazzalunga[3,*], F. Riccobono[1,#], F. Taccetti[2], G. Valli[1], R. Vecchi[1]

[1]Department of Physics, Università degli Studi di Milano and INFN, Milan, 20133, Italy
[2]Dept. of Physics and Astrophysics, Università degli Studi di Firenze and INFN, Sesto Fiorentino, 50019, Italy
[3]Dept. of Inorganic, Metallorganic, and Analytical Chemistry, Università degli Studi di Milano, Milan, 20133, Italy
* now at: Dept. of Environmental and Territorial Sciences, University of Milan-Bicocca, Milan, 20122, Italy
[#]now at: Laboratory of Atmospheric Chemistry, Paul Scherrer Institut, Villigen PSI, 5232, Switzerland

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Presenting author email: vera.bernardoni@unimi.it

Carbon is one of the main constituents of atmospheric aerosol. The study of carbonaceous aerosol is important because of its adverse effects on health, air quality, visibility, and Earth's radiation balance. In this context, the development of analytical and modelling techniques aiming at the identification of natural and anthropogenic contributions gains great importance.

^{14}C measurement on total carbon (TC) is a good tool for fossil/non fossil sources separation (Hildemann et al., 1994). However, wood burning has to be considered mainly of anthropogenic origin at mid-latitudes. Therefore, ^{14}C measurements on TC do not allow the complete natural/anthropogenic contributions separation.

^{14}C measurements on organic and elemental carbon (OC and EC, respectively) allow a distinction between the wood/biomass burning and the biogenic source, provided that the OC/EC emission ratio for wood/biomass burning is known. This model is limited by the difficulty in the assessment of the secondary contribution from wood/biomass burning (Szidat et al., 2009), as the OC/EC emission ratio measured at the source cannot correctly account for secondary aerosol formation. Moreover, ^{14}C measurements for the fraction of modern carbon (f_m) determination must be carried out on each carbon fraction after a suitable isolation. At the state of art EC and OC are operationally defined. Therefore, a key point of ^{14}C measurements on carbon fractions is the thermal separation of OC and EC.

This work aimed at gaining information on the effects of different thermal treatments on ^{14}C measurements of organic (OC) and elemental (EC) carbon fractions in the atmospheric aerosol. Improvements to the traditional approaches for the determination of the f_m(OC) and f_m(EC) are proposed and tested using a devoted sample preparation line (Calzolai et al., 2011).

f_m(EC) determination is usually carried out after EC isolation using a single oxygen combustion step. In this work, we show that the most refractory OC fraction cannot be efficiently removed by the oxygen treatment alone without significantly affecting the EC recovery. Therefore, we propose to use a Helium combustion step at high temperature in addition to the oxygen treatment. Our tests demonstrate that the addition of a high temperature He step (optimised temperature setting: 750 °C) to the oxygen treatment (375°C, 40 min) is effective in removing the refractory OC.

The direct determination of f_m(OC) can be difficult because of possible OC pyrolysis, which can be reduced by water soluble components removal. Therefore, here we propose to determine f_m(OC) measuring either the fraction of modern carbon of TC and EC or the fraction of modern carbon of water soluble (f_m(WSOC)) and water insoluble (f_m(WINSOC)) organic carbon. Tests on the equivalence of the approaches have shown good agreement.

Our tests were carried out on PM10 samples collected in a heavily polluted urban area (Milan, Italy) during wintertime. f_m(OC), f_m(EC), and f_m(TC) values obtained in our tests were then used to attempt a preliminary source apportionment using ^{14}C measurements (Figure 1).

The wood burning primary contribution to OC was evaluated from both ^{14}C and levoglucosan using tailored emission factors (Piazzalunga et al., 2011). A good agreement between the approaches was found and wood burning primary contribution accounted for about 18% of OC in Milan during wintertime. Secondary OC from biomass burning and the contribution from other urban sources were tentatively identified following literature approaches, with the aim of evaluating the biogenic contribution to OC, which was estimated to be about 18%.

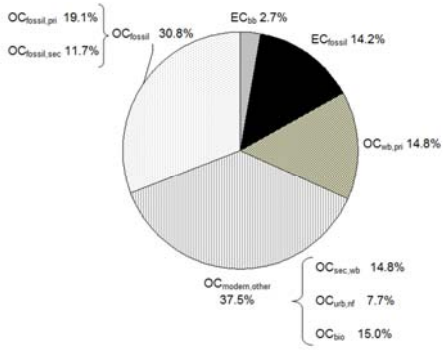

Figure 1. TC source apportionment in Milan – Italy.

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