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Characteristics of carbonaceous aerosols in Emilia-Romagna (Northern Italy) based on two fall/winter field campaigns

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ABSTRACT

The carbonaceous aerosol in Emilia-Romagna region (Northern Italy) was characterized in two fall/winter monitoring campaigns conducted through the years 2011–2012 and 2012–2013. Nearly 650 $PM_{2.5}$ samples were collected at three monitoring stations describing urban background (main city Bologna, MS, Parma and Rimini) and one rural background site (San Pietro, SP). OC and EC values were measured by the thermal–optical transmittance method (TOT). Low flow-rate sampling strategy (24 m^3 air volume per day) was used to reduce loading of light absorbing material on the filter surface in order to ensure the correct OC/EC discrimination.
The TC values measured in winter 2011–2012 ranged from 9.8 μgC m^{-3} at San Pietro to 12.0 μgC m^{-3} at Parma, consisting of OC from 8.6 μgC m^{-3} at SP to 9.9 μgC m^{-3} at MS and EC from 1.3 μgC m^{-3} at SP to 2.5 μgC m^{-3} at Rimini. In winter 2012–2013, lower values were in general found with TC values ranging from 7.8 to 9.1 μgC m^{-3} consisting of OC from 5.1 to 7.0 μgC m^{-3} and EC from 1.5 to 2.2 μgC m^{-3}.
Such differences can be likely explained by higher pollutant emissions related to domestic heating in colder fall/winter 2011/2012 (mean temperature ≈ 2 °C in comparison with ≈ 7 °C in winter 2012/2013). This hypothesis is supported by high levels of levoglucosan, as unambiguous tracer for biomass burning emission, and of polycyclic aromatic hydrocarbons related to combustion (levoglucosan ≈ 1000 ng m^{-3} and burning PAHs ≈ 4 ng m^{-3} at MS and SP sites).

1. Introduction

Carbonaceous aerosol is an ubiquitous and important component of the fine atmospheric particulate matter (PM) which accounts for 20–45% of $PM_{2.5}$ at European rural and urban background sites (Yttri et al., 2007; Putaud et al., 2010; Perrone et al., 2012; Jedynska et al., 2014; Sandrini et al., 2014). In recent years there is increasing evidence of its role in global climate change and radiative budget, involvement in heterogeneous reactions, and possible content of mutagenic and carcinogenic components (Reche et al., 2011; Bond et al., 2013; Perrone et al., 2013). In this context, among the thousands of organic components present in the atmospheric aerosol, elemental (EC) and organic carbon (OC) are usually quantified as more generic indicators of air quality to identify pollution sources and assess their environmental impact (Sillanpää et al., 2005; Andreae and Gelencsér, 2006; Wallén et al., 2010; Cheng et al., 2011; Pio et al., 2011; Jedynska et al., 2014; Zhao et al., 2011). EC is the inert matter with graphitic-like structure released from incomplete combustion of fossil fuels in transportation, heating, and power generation, and of wood and biomass in residential heating and agriculture activities. OC in contrast is an aggregate of organic compounds, such as aliphatic and aromatic hydrocarbons, that are either directly released in the atmosphere by primary sources or secondarily formed in the atmosphere from anthropogenic or biogenic precursors.

For this reason, the characterization of the carbonaceous aerosol was included in the Supersito project for a chemical and physical characterization of atmospheric aerosol in Emilia-Romagna (Northen Italy) (ARPA-EMR, 2012). This region is located at the Eastern side of the Po Valley, the most industrialized and trafficked area in Italy, which is recognized as one of the most air polluted situations in Europe, in particular during the cold seasons, when enhanced anthropogenic emissions from residential heating combined with stagnant atmospheric conditions result into the pollutant accumulation near the source locations (Carbone et al., 2010; Bernardoni et al., 2011; Belis et al., 2011; Bigi et al., 2012; Perrone et al., 2012; Piazzalunga et al., 2013a; Pietrogrande et al., 2013, 2014a; Perrino et al., 2014; Decesari et al., 2014).

This study concerns nearly 650 $PM_{2.5}$ samples collected in two monitoring campaigns during fall/winter periods in 2011–2012 and 2012–2013 at four urban and rural locations in the region.

In this work the thermal–optical transmittance method (TOT) was used, as one of the most widely recognized methods for measuring OC and EC in atmospheric particulates (Yang and Yu, 2002; Chow et al., 2004; Bae et al., 2004; Han et al., 2007; Boparai et al., 2008; Cheng

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et al., 2011; Piazzalunga et al., 2011; Chow et al., 2011; Cheng et al., 2012; Bautista et al., 2015). Up to date however, there is no standard protocol of analysis and the definition of OC and EC is operative and therefore depending on the technique used. In this work, the EUSAAR2 protocol (European Supersites for Atmospheric Aerosol Research) was employed as recently suggested for samples collected at European regional sites (Cavalli et al., 2010; CEN, 2011; Piazzalunga et al., 2013a).

The most suitable sampling protocol was selected to provide reliable results as applied to aerosol samples collected in a heavily polluted area, as Emilia-Romagna region in winter, that are characterized by high loading of carbonaceus material on the filters.

Further information on the concentration of polycyclic aromatic hydrocarbons and levoglucosan, as markers related to biomass burning, were evaluated in order to give insigth into the potential contribution of wood combustion to influence the thermal behavior of the carbonaceous species.

2. Materials and methods

2.1. Aerosol sampling

The duration of the two monitoring campaigns was from 15th November 2011 to 29th March 2012 and from 1st October 2012 to 31st March 2013. Samples were collected at four monitoring stations of Emilia-Romagna ARPA agency (Region Agency for Prevention and Environment), describing different emission situations in the region, i.e., three urban background sites, a main site in Bologna, (MS), two satellite sites in Parma and Rimini, and one rural background site (San Pietro Capofiume). The urban sites are located in different parts of the Emilia-Romagna region, characterized by significant agricultural and industrial activities and the presence of main arterial roads. MS is located in the city of Bologna—which is the most populous city in the region (over 380,000 inhabitants), Parma—with about 190,000 inhabitants, is situated half-way between Milan to Bologna—and Rimini, with about 150,000 inhabitants, is located on the coast of the Adriatic Sea, and therefore visited by many tourists during holidays and week-ends. The rural background station of San Pietro Capofiume, SP, is located on a flat, homogeneous terrain of harvested fields, 40 km north-east from Bologna: it represents the typical low land agricultural areas with sparse towns and villages.

In the framework of the Supersito project, the $PM_{2.5}$ samples were collected on quartz fiber filters (PALL Tissu Quartz 2500 QAO-UP 2500 filters, 47 *mm* of diameter) with automatic outdoor stations at MS, SP, Rimini and Parma sites. A low volume sampler (Skypost PM, TCR TECORA Instruments, Corsico, Milan, Italy) operated at the standard flow rate of 38.3 $Lmin^{-1}$ to collect an air volume of 55 m^3 per day. In addition, the sampler has been properly modified to reduce air flow rate to 16.7 $Lmin^{-1}$ and collect an air volume of 24 m^3 per day. Instrument details and validation of the modified procedure are reported in Supplementary Material.

In the framework of the ARPA-ER air quality monitoring, PM samples are routinely collected in urban areas, including Bologna, Rimini, and Parma, and the rural background San Pietro, using low volume sequential samplers (Swam 5C, FAI Instruments, Roma) to monitor PM_{10} and/or $PM_{2.5}$ concentration on daily basis and measure concentrations of some PAHs in PM_{10} on monthly basis.

After sampling, filter equilibration and weighing was performed following the procedure outlined in the European Standard EN 12341 (CEN, 1998). The quartz fiber filters were heated for 3 h at 800 °C in air before use, to reduce their carbon blank. Thus, the background concentration in the quartz fiber filter and matrix, which could influence the analysis, was minimized.

2.2. Thermal–optical transmission analysis

The samples were analyzed in the ARPA laboratory using a Sunset Laboratory Thermal/Optical Carbonaceous Aerosol Analyzer (Laboratory Inc). The carbon analyzer was routinely checked for leaks and operated using Ultra-High Purity (Grade 6.0) Helium gas. The instrument was calibrated prior to use with injections of sucrose standard solution (concentration of 10 gL^{-1} corresponding to 42 $\mu gC\ cm^{-2}$ of organic carbon on the filter surface).

According to the used thermal protocol EUSAAR2 (Cavalli et al., 2010), the carbonaceous material (OC) is initially thermally desorbed in an inert atmosphere (99.999% pure He) at relatively low temperature in four steps (200 °C for 120 s; 300 °C for 150 s; 450 °C for 180 s; 650 °C for 180 s). Then desorption is performed to evolve the EC component at higher temperature in four steps (500 °C for 120 s; 550 °C for 120 s; 700 °C for 70 s; 850 °C for 80 s) in an oxidizing atmosphere (2% oxygen/98% helium final mixture in the sample oven). During this stage, organic compounds are vaporized and catalytically oxidized to carbon dioxide but also a percentage of native elemental carbon may be pyrolytically converted into elemental carbon (Pyrolytic Carbon, PC) and therefore interfere in the determination of EC. In order to correct this potential bias, the laser beam transmission through the sample is monitored during the analysis and the point at which the laser transmission returns to the original pre-pyrolysis value is used to define the split between organic and elemental carbon (split point). A premature evolution of light-absorbing carbon containing EC before the EC/OC split will lead to underestimate the EC amount (Chow et al., 2004; Subramanian et al., 2006; Yang and Yu, 2002; Boparai et al., 2008).

2.3. Elemental analysis

Elemental analysis was performed in the laboratory of the University of Ferrara, Department of Chemistry and Pharmaceutical Sciences, using a Thermo Scientific 2000 CHNSO Analyzer equipped with a thermal conductivity detector (TCD). For each measurement a material amount ranging from 2 to 5 mg was obtained by cutting proper portions of the PM filters. After introduction in the tin capsule, the sample was weighed and put into the combustion reactor using an autosampler.

3. Results and discussion

3.1. Quality assurance of the Thermal Optical Transmittance method

In this work the analytical performance of a thermo–optical-transmission analyzer was assessed for precision, linearity and limits of quantification in order to find out the proper protocol providing a reliable OC/EC quantification in PM samples.

The procedure assured good precision and sensitivity: relative standard deviation RSD% were 5.2%, 6.5% and 3.9% for OC, EC and TC values, respectively, and limits of quantification were 3 $\mu gC\ cm^{-2}$ for OC—corresponding to 0.7 $\mu gC\ m^{-3}$ and 1.6 $\mu gC\ m^{-3}$, collecting 55 m^3 and 24 m^3 air volume, respectively—and 0.4 $\mu gC\ cm^{-2}$ for EC—corresponding to 0.1 $\mu gC\ m^{-3}$ (55 m^3) and 0.2 $\mu gC\ m^{-3}$ (24 m^3).

In addition, the reliability of the Total Carbon measurements was validated by intercomparison with data obtained by the elemental CHNSO Analyzer, as a different independent instrument which guarantees routine and high capacity analyses (Fellner et al., 2011; Zhao et al., 2011). In general a close agreement was obtained between the values measured with the two techniques, characterized by a mean percentage difference $\approx 6\%$ (Table 1), that is a meaningful evidence of the reliability of the used TOT procedure to obtain accurate TC determinations. The detailed investigation is reported in the Supplementary material.

3.2. Quantification of OC and EC carbonaceous fractions

In the early part of the first monitoring campaign from 15th November 2011 to 13th February 2012 an air volume of 55 m^3 was collected at the four sampling sites and analyzed for EC, OC and TC (computed as the sum EC + OC). The measured EC values were plotted as a function of TC concentrations to highlight the influence of the filter loading on the TOT