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Short-term secondary organic carbon estimations with a modified OC/EC primary ratio method at a suburban site in Madrid (Spain)

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ABSTRACT

A time series of more than two years of continuous measurements of EC, OC and TC obtained with a Rupprecht and Patashnick (R&P) thermal analyzer at a suburban site in Madrid has been evaluated in this work. Correction factors obtained from intercomparison exercises with thermo-optical methods were applied to the original measurements. Corrected OC and EC mean values are 3.7 and 1.3 μg m^{-3} respectively. The highest individual values have been recorded in winter. No seasonal variation has been observed in OC, whereas a slight decrease of EC is observed in summer, leading to higher OC/EC ratios. The mean value of the OC/EC ratio is 4.9. Daily patterns show maximum EC and OC associated to traffic rush hours, with a delay of the OC peak related to the formation of SOC. Daily oscillation is more pronounced in winter. Hourly estimations of SOC production have been obtained by the primary OC/EC ratio approach, after discounting the OC, EC background contamination. A mean primary ratio value of 0.59 has been used for SOC short-term estimations throughout the entire time period. As expected, the highest SOC production is observed in summer, related to the increasing in photochemical activity, which also influences daily patterns and the time of the daily SOC maximum. In summer the daily SOC production ranges from 80 to 92%, whereas in the winter months it varies from 70 to 84%. These SOC estimations do not discount primary biogenic or natural contributions to OC and are therefore maximum values.

1. Introduction

Carbonaceous matter is a major component of ambient atmospheric aerosol being mainly associated to fine particles and to natural and anthropogenic combustion sources. In recent years, results from experimental studies in the US have observed contributions of up to 60% of this aerosol component to the total fine particle mass (Malm et al., 2004). In Europe, Putaud et al. (2004) and Querol et al. (2004a, 2008) reported contributions between 20–40 and 25–50% to the ambient PM_{10} and $PM_{2.5}$ mass, respectively. The values depended on the characteristics and influence of pollution sources at measurement sites, but climatic and geographic features could also account for some of the observed variations (Querol et al., 2009). Daily concentrations of ambient carbon aerosol reaching 80% of the total $PM_{2.5}$ mass have been recorded in Madrid coinciding with episodes of peak PM concentrations (Artíñano et al., 2004).

The carbonaceous fraction is by far the least understood and most difficult to characterize, quantify and source apportion of the ambient aerosol constituents. The large number (>100 or up to 1000) of organic compounds present in aerosol particles, apart from the occurrence of positive and negative artifacts from gaseous organic compounds in filter-based methods (Cheng et al., 2009), definitely contributes to the difficulties associated with their study. The total carbon (TC) in the aerosol can be divided into: elemental carbon (EC), inorganic carbon (IC) and organic carbon (OC). EC is directly emitted from incomplete combustion and can be both anthropogenic (combustion of fossil or wooden fuels) and natural (wild fires). IC can be found in crust material present mainly in coarse aerosol particles. OC is the carbon content of a mixture of non-volatile and semi-volatile organic compounds in various oxidation states. It originates from a wide range of sources, both anthropogenic and natural, and can be either emitted by primary sources (primary organic aerosol – POA) or originated through different processes. These can be both adsorption of semi-volatile

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primary gaseous organic material and condensation of low-volatility products from the photo-oxidation of volatile organic compounds (VOCs) (secondary organic aerosol – SOA).

Global models predict that urban sources of organic aerosol are small compared with biomass burning emissions and SOA formation (Kanakidou et al., 2005). Nevertheless, several recent studies have found organic aerosol to be well correlated with tracers of urban pollution, suggesting that the influence of urban emissions may be larger than previously recognized (de Gouw et al., 2005). These studies showed that the good correlation is not due to POA emissions, but instead to a rapid growth of SOA in urban air that overwhelms the direct POA emissions within a few hours of photochemical processing. Aside from the relevant effects of carbonaceous aerosol on local and regional air quality, a number of recently published works have shown how this type of aerosol plays a crucial role in many environmental issues at a global scale (Bond and Sun, 2005; Ulbrich et al., 2009; Jiménez et al., 2009).

Availability of data sets with a high time resolution is fundamental for the understanding of sources and processes affecting the evolution of carbonaceous aerosol components. The present study is aimed at analyzing the temporal variations of hourly EC and OC measurements performed with a thermal semi-continuous analyzer at a suburban site in Madrid from 2006 to 2008. This type of analyzer has been used in numerous works to obtain EC and OC concentrations (Höller et al., 2002; Kristensson et al., 2004; ten Brink et al., 2005; Jones and Harrison, 2005; Plaza et al., 2006; Quincey et al., 2009; Zhang et al., 2009), although it presents some limitations inherent to the techniques employed to measure the different carbonaceous fractions (Even et al., 2000). For this reason, an evaluation and further correction of the EC and OC concentrations data set obtained during this period was carried out according to the results of intercomparison exercises performed against other measurement methods less prone to interferences.

EC and OC concentrations have been assessed in terms of monthly/seasonal variations and daily patterns have been analyzed under different atmospheric dispersion conditions. Availability of hourly resolved data permitted to follow the evolution of the carbonaceous aerosol components in the reactive urban air throughout the day and especially after emission peak periods. This paper proposes an innovative approach to differentiate secondary from primary organic carbon. Instead of the classic methodology of using minimum OC/EC ratio values taken from daily averaged concentrations we used moments of rapidly increasing EC concentrations to estimate the true values for primary urban traffic OC/EC ratios, after discounting OC and EC background urban contamination. The observed seasonal and morning–evening differences in calculated traffic OC/EC primary ratios have been discussed in terms of the dilution conditions.

Finally, using this primary ratio approach an apportionment of measured OC into primary and secondary origins has been performed. This is suitable in areas with a predominant carbon aerosol source. The results of daily patterns for secondary organic carbon estimations and monthly variations are discussed in this work.

2. Sampling site and measurements

2.1. Description of the monitoring site

Particulate carbon measurements were performed at the CIEMAT facilities located in Ciudad Universitaria, a non-residential area (40°27′23″N, 3°43′32″W, 669 m ASL) in the Madrid NW city outskirts. This site can be considered representative of the urban background and is located downwind of the centre of Madrid for the N to SW wind directions (clockwise), and downwind of a great forested area with respect to the W and NW wind directions. In the Madrid region there are no significant heavy industrial atmospheric pollution emission sources. Thus, traffic exhaust and commercial and residential heating installations (natural gas, fuel–oil and some coal boilers) in winter are the major atmospheric pollution emitters in the metropolitan area (6 million inhabitants). With respect to traffic, the fraction of diesel passenger cars has been climbing steadily in the last ten years, currently representing more than 50% of the vehicular fleet.

The main atmospheric environmental problems in this area are related to the occurrence of pollution episodes that usually take place during the fall and winter cold months, and are associated to atmospheric stagnation conditions (Pujadas et al., 2000). In summer there are occasional events of photochemical pollution (Plaza et al., 1997). Additionally, high atmospheric particle concentrations can be recorded during long-range transport events, mainly in spring and summer, related to African dust outbreaks that can cause severe impacts on the coarser fraction of ambient particle concentrations (Artíñano et al., 2003). Locally re-suspended dust and regional air recirculation can also contribute to increase the PM_{10} levels in these seasons (Querol et al., 2004a,b; Salvador et al., 2008).

2.2. Measurements and instrumentation

A number of studies have been published in the recent years based on measurements discriminating EC and OC from carbonaceous aerosol in ambient air. Most of them are based on sampling devices that collect particles over filters which are subsequently analyzed by thermo-optical techniques, a procedure that in some cases can be automated. These filter-based techniques are subjected to several positive and negative artifacts affecting the OC fraction which have been studied widely (Chow et al., 2001; Viidanoja et al., 2002; Lim et al., 2003; Viana et al., 2006). Several uncertainties associated with the ambient conditions and the artifacts produced during sampling are related to the adsorption of organic carbon onto the filters and deposited particles, or its volatilization. Interferences by adsorption of VOCs in the filter substrate are more important during short-term sampling. After some time the active sites in the filter substrates become saturated and adsorption is reduced. On the contrary adsorption/desorption from deposited particles is probably more important during long term sampling because the atmospheric conditions are more variable The quantification of these artifacts may depend on the sampling instrumentation and the filter type (EMEP, 2004; ten Brink et al., 2004; Viana et al., 2006). The use of denuders can reduce positive artifacts (Polidori et al., 2006), but then special attention must be paid to volatilisation losses of OC caused by the broken equilibrium conditions. The thermo-optical technique, usually implemented in laboratory instruments, is based on OC thermal decomposition in absence of oxygen and EC combustion, using different temperature evolutions and atmospheres (Birch, 1998). Further reduction/oxidation of evolved gaseous compounds, depending on the implemented analytical detection, is also necessary. Pyrolized OC is usually distinguished from EC by following the filter reflectance/transmittance under a laser beam. The main inaccuracy of this method is associated with the correct separation between EC and pyrolized OC, so that slight deviations in the split point can produce perceptible errors when determining the EC fraction (Subramanian et al., 2006).

In this work, continuous measurements of the EC and OC fractions from the carbonaceous aerosol were carried out by a thermal analyzer (Ambient Carbonaceous Particle Monitor-ACPM, Rupprecht and Patashnick model 5400, Thermo Scientific Inc.). The most advantageous aspect of the ACPM instrument is its ability to provide semi-continuous EC and OC concentrations with a high