Atmospheric Environment 99 (2014) 587–598

Contents lists available at ScienceDirect

Atmospheric Environment

journal homepage: www.elsevier.com/locate/atmosenv

Spatial and seasonal variability of carbonaceous aerosol across Italy

Silvia Sandrini [a,*], Sandro Fuzzi [a], Andrea Piazzalunga [b], Paolo Prati [c], Paolo Bonasoni [a], Fabrizia Cavalli [d], Maria Chiara Bove [c], Mariarosaria Calvello [e], David Cappelletti [f], Cristina Colombi [g], Daniele Contini [h], Gianluigi de Gennaro [i], Alessia Di Gilio [i], Paola Fermo [j], Luca Ferrero [k], Vorne Gianelle [g], Michele Giugliano [l], Pierina Ielpo [h,m], Giovanni Lonati [l], Angela Marinoni [a], Dario Massabò [c], Ugo Molteni [j,1], Beatrice Moroni [f], Giulia Pavese [e], Cinzia Perrino [n], Maria Grazia Perrone [k], Maria Rita Perrone [o], Jean-Philippe Putaud [d], Tiziana Sargolini [n], Roberta Vecchi [p], Stefania Gilardoni [a]

[a] *Institute for Atmospheric Sciences and Climate (ISAC), National Research Council (CNR), 40129 Bologna, Italy*
[b] *Department of Environmental Sciences, Milano-Bicocca University, 20126 Milan, Italy*
[c] *Department of Physics & INFN, University of Genoa, 16146 Genoa, Italy*
[d] *European Commission, JRC, Institute for Environment & Sustainability, 21027 Ispra, VA, Italy*
[e] *IMAA – National Research Council, 85050 Tito Scalo, PZ, Italy*
[f] *SMAArt & Department of Biology and Biotechnology, University of Perugia, 06125 Perugia, Italy*
[g] *ARPA Lombardia, Regional Centre for Air Quality Monitoring, 20122 Milano, Italy*
[h] *Institute for Atmospheric Sciences and Climate (ISAC), National Research Council (CNR), 73100 Lecce, Italy*
[i] *Department of Chemistry, University of Bari "Aldo Moro", 70126 Bari, Italy*
[j] *Department of Chemistry, University of Milan, 20133 Milan, Italy*
[k] *Polaris Research Center, DISAT, University of Milano-Bicocca, 20126 Milano, Italy*
[l] *Politecnico di Milano, D.I.C.A. Environmental Section, 20133 Milano, Italy*
[m] *Water Research Institute – National Research Council (CNR), 70123 Bari, Italy*
[n] *Institute of Atmospheric Pollution Research (IIA), National Research Council (CNR), 00015 Rome, Italy*
[o] *Mathematics and Physics Department, University of Salento, 73100 Lecce, Italy*
[p] *Physics Department & INFN, University of Milan, 20133 Milan, Italy*

HIGHLIGHTS

- We compared OC and EC data from different sites across the Italian Peninsula.
- OC and EC concentration maxima occur during winter and minima during summer at all except remote sites.
- Higher OC levels characterize the Po Valley compared to the rest of Italy both during summer and winter.
- Biomass burning for residential heating strongly affects winter OC concentrations in the Po Valley.
- Carbonaceous matter contribution to $PM_{2.5}$ ranges between 37% at rural and 47% at traffic sites, on an annual basis.

ARTICLE INFO

Article history:
Received 22 July 2014
Received in revised form
14 October 2014
Accepted 15 October 2014
Available online 16 October 2014

Keywords:
Particulate matter
Organic carbon

ABSTRACT

This paper analyses elemental (EC), organic (OC) and total carbon (TC) concentration in $PM_{2.5}$ and PM_{10} samples collected over the last few years within several national and European projects at 37 remote, rural, urban, and traffic sites across the Italian peninsula.

The purpose of the study is to obtain a picture of the spatial and seasonal variability of these aerosol species in Italy, and an insight into sources, processes and effects of meteorological conditions.

OC and EC showed winter maxima and summer minima at urban and rural locations and an opposite behaviour at remote high altitude sites, where they increase during the warm period due to the rising of the Planetary Boundary Layer (PBL). The seasonal averages of OC are higher during winter compared to summer at the rural sites in the Po Valley (from 1.4 to 3.5 times), opposite to what usually occurs at rural

* Corresponding author. Institute for Atmospheric Sciences and Climate (ISAC), National Research Council (CNR), Via Gobetti, 101, 40129 Bologna, Italy.
E-mail address: s.sandrini@isac.cnr.it (S. Sandrini).
[1] Present address: Paul Scherrer Institute, Villigen, Switzerland.

http://dx.doi.org/10.1016/j.atmosenv.2014.10.032
1352-2310/

Elemental carbon
OC/EC ratio
SOA

locations, where OC increases during the warm period. This denotes the marked influence of urban areas on the surrounding rural environment in this densely populated region.

The different types of sites exhibit marked differences in the average concentrations of carbonaceous aerosol and OC/EC ratio. This ratio is less sensitive to atmospheric processing than OC and EC concentrations, and hence more representative of different source types. Remote locations are characterised by the lowest levels of OC and especially EC, with OC/EC ratios ranging from 13 to 20, while the maximum OC and EC concentrations are observed at road-traffic influenced urban sites, where the OC/EC ratio ranges between 1 and 3. The highest urban impacts of OC and EC relative to remote and rural background sites occur in the Po Valley, especially in the city of Milan, which has the highest concentrations of PM and TC and low values of the OC/EC ratio.

1. Introduction

The carbonaceous fraction is an important component of the fine atmospheric particulate matter (PM) which accounts for 20–45% of $PM_{2.5}$ and somewhat less (20–35%) of PM_{10} on an annual basis (Putaud et al., 2010; Yttri et al., 2007). Carbonaceous aerosol is composed by OC and a refractory light-absorbing component generally referred to as soot (Baumgardner et al., 2012; Bond and Bergstrom, 2006). Soot is generated by incomplete combustion of organic material from traffic, residential heating, industrial activities and energy production using heavy oil, coal or biofuels. Depending on its empirical determination, soot is reported as elemental carbon (EC) or equivalent black carbon (EBC). EC is quantified by thermal–optical methods, while EBC is derived from optical measurements. In the atmosphere, soot is always associated with other substances from combustion sources, including OC. The sum of OC and EC is known as total carbon (TC). Soot has a primary origin, while OC can be both primarily emitted but also formed in the atmosphere through condensation to the aerosol phase of low vapour pressure compounds emitted as primary pollutants or formed in the atmosphere (Gentner et al., 2012; Robinson et al., 2007). As a result of this, the ratio of particulate OC to EC differs widely, both in space and seasonally, being influenced by primary emission sources, different OC and EC removal rates by deposition, OC phase partitioning, and secondary organic aerosol (SOA) formation and/or reactivity.

The occurrence in the atmosphere of both OC and EC is relevant from both climatic and human health standpoints, which explains the increasing scientific interest in monitoring these chemical species (Bond et al., 2013; Janssen et al., 2011). Although EC represents generally a minor component in terms of mass of the atmospheric fine aerosol, it is the major absorber of visible light, and a driver of global warming, whereas most OC can contribute to warming or scattering depending on functional group composition and mixing with soot particles (Bond and Bergstrom, 2006).

In recent years, a number of epidemiological studies have highlighted the link between short-term and long-term exposure to PM and a broad range of human health impacts, including respiratory and cardiovascular effects as well as premature deaths (WHO, 2012). EC has been suggested as a better proxy for harmful PM from combustion sources, especially from diesel exhaust, than undifferentiated PM (Janssen et al., 2011), although the harmful components might also be other species associated to EC particles (Mills et al., 2011).

A growing consensus is such emerging towards the formulation of an EC-$PM_{2.5}$ standard, including this species in the list of monitored/regulated pollutants, as an important tool for evaluating traffic pollution impacts in urban areas (Grahame and Schlesinger, 2010; Reche et al., 2011).

The present paper aims at providing a large-scale investigation of the average concentrations of OC, EC and TC over the Italian peninsula and at exploring their spatial and seasonal variability under the influence of several controlling factors, i.e. type and strength of the sources and meteorological conditions.

The Italian territory, excluding the islands, is topographically and climatically subdivided into two regions: Continental Italy and Peninsular Italy (Fig. 1).

Continental Italy, in the north, includes the broad, triangle-shaped North Italian Plain (Po Valley) and the high mountain chain of the Alps, and is characterized by a climate similar to continental Europe, with cold winters, distinct differences between seasons, low wind speed and frequent stable atmospheric conditions, especially during winter. The Po Valley, due to the high density of anthropogenic sources, and the orographic and meteorological characteristics particularly unfavourable for pollutants dispersion, is known as a hot spot in Europe in relation to air quality (Carbone et al., 2010; Ferrero et al., 2011).

Peninsular Italy, encompassing all the Italian peninsula south of the junction of the Ligurian Alps with the Apennines, generally fits the Mediterranean climate profile, with higher wind speed and stable atmospheric conditions during summertime.

In spite of the increasing number of OC and EC measurements carried out in Italy in recent years, their spatial distribution is still rather inhomogeneous, with some areas, especially in Central and Southern Italy, still lacking data, and the Po Valley quite extensively monitored. Though a larger number of measurements of the aerosol carbonaceous component were available, the choice in this study has been restricted to data obtained by the thermal–optical method, which provides comparable data. This study represents the first analysis of carbonaceous aerosol data across the Italian territory as a whole.

2. Sampling and analysis

2.1. Sampling

The present database of OC, EC and TC measurements includes data collected during the years 2005–2012 at 37 sites spread along the Italian peninsula (Fig. 1). Only one measurement campaign (MI Mes) dates back to the years 2002–2003. The monitoring stations include industrial, traffic, urban, semi-rural, rural and remote locations, classified on the basis of their distance from pollution sources according to criteria proposed by the European Environment Agency (Larssen and Helmis, 1999). At 32 sites the $PM_{2.5}$ fraction was analysed, in some cases simultaneously to PM_{10} data, while at 5 sites, only PM_{10} data were available. PM mass concentration was measured gravimetrically at all sites, with the exception of RM Ada, MLB and FE Cas where beta attenuation online monitors were employed. Table 1 summarizes the complete list of