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Veneto region (NE Italy)**

Md. Badiuzzaman Khan^a, Mauro Masiol^b,
Gianni Formenton^c, Alessia Di Gilio^{d,e},
Gianluigi de Gennaro^{d,e}, Claudio Agostinelli^a,
Bruno Pavoni^{a*}

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CARBONACEOUS PM_{2.5} AND SECONDARY ORGANIC AEROSOL ACROSS THE VENETO REGION (NE ITALY)

**Md. Badiuzzaman Khan^a, Mauro Masiol^b,
Gianni Formenton^c, Alessia Di Gilio^{d,e},
Gianluigi de Gennaro^{d,e}, Claudio Agostinelli^a,
Bruno Pavoni^{a*}**

^a**Dipartimento di Scienze Ambientali
Informatica e Statistica, Università Ca' Foscari Venezia
Dorsoduro 2137, 30123 Venezia, Italy**

^b**Division of Environmental Health and Risk Management
School of Geography, Earth and Environmental Sciences
University of Birmingham
Edgbaston, Birmingham B15 2TT
United Kingdom**

^c**Dipartimento Provinciale di Padova
Agenzia Regionale per la Prevenzione e Protezione Ambientale del Veneto
(ARPAV), Via Ospedale 22, 35121 Padova, Italy**

^d**Agenzia Regionale per la Prevenzione e Protezione Ambientale della Puglia
(ARPAP), Corso Trieste 27, 70126 Bari, Italy**

^e**Dipartimento di Chimica, Università degli Studi di Bari, Via Orabona 4, 70126,
Italy**

- (*) Corresponding Author: brown@unive.it

ABSTRACT

Organic and elemental carbon (OC-EC) were measured in 360 PM_{2.5} samples collected from April 2012 to February 2013 at six provinces in the Veneto region, to determine the factors affecting the carbonaceous aerosol variations. The 60 daily samples have been collected simultaneously in all sites during 10 consecutive days for 6 months (April, June, August, October, December and February). OC ranged from 0.98 to 22.34 µg/m³, while the mean value was 5.5 µg/m³, contributing 79% of total carbon. EC concentrations fluctuated from 0.19 to 11.90 µg/m³ with an annual mean value of 1.31 µg/m³ (19% of the total carbon). The monthly OC concentration gradually increased from April to December. The EC did not vary in accordance with OC. However the highest values for both parameters were recorded in the cold period. The mean OC/EC ratio is 4.54, which is higher than the values observed in most of the other European cities. The secondary organic carbon (SOC) contributed for 69% of the total OC and this was confirmed by both the approaches OC/EC minimum ratio and regression. The results show that OC, EC and SOC exhibited higher concentration during winter months in all measurement sites, suggesting that the stable atmosphere and lower mixing play important role for the accumulation of air pollutant and hasten the condensation or adsorption of volatile organic compounds over the Veneto region. Significant meteorological factors controlling OC and EC were investigated by fitting linear models and using a robust procedure based on weighted likelihood, suggesting that low wind speed and temperature favour accumulation of emissions from local sources. Conditional probability function and conditional bivariate probability function plots indicate that both biomass burning and vehicular traffic are probably the main local sources for carbonaceous particulate matter emissions in two selected cities.

Keywords: PM_{2.5}, Organic carbon, Elemental carbon, Meteorological factors, Secondary organic aerosol, Long-range transport, Po Valley

1. INTRODUCTION

Carbonaceous compounds account for an important fraction of atmospheric particulate matter (PM), generally contributing between 30 and 50% of PM with aerodynamic diameter $< 2.5 \mu\text{m}$ ($\text{PM}_{2.5}$) in many European urban areas (Putaud et al., 2004). In the recent years, the scientific community has paid much attention to the carbonaceous fraction of PM, since it may affect the global radiation budget, cloud microphysics (Seinfeld and Pandis, 1998; Lyamani et al., 2006) and has effects on the global climate change (Hitzenberger et al., 1999; Dan et al., 2004). In addition, increased levels of urban carbonaceous PM are significantly associated with cardiovascular mortality and morbidity (Na et al., 2004; Ito et al., 2011) and several organic compounds of known or suspected carcinogenic and/or mutagenic potential are commonly found in PM, e.g., polycyclic aromatic hydrocarbons (PAHs) and polychlorinated biphenyls (PCBs) (WHO, 2000).

The carbonaceous PM is composed of a refractory component, commonly called elemental carbon (EC) and an organic fraction (OC). EC is a primary pollutant being mainly released in particle-phase from the incomplete combustion of carbon-containing fuels. On the contrary, OC includes thousands of different organic compounds (e.g., aliphatic, aromatic hydrocarbons, carboxylic acids and carboxylic compounds with polar substituent, etc.) with widely varying chemical and physical properties, such as molecular weights, level of oxidations and gas-particulate partitioning. OC can be directly emitted as a primary OC from many sources including combustions, industrial emissions, geological and natural sources. It can also form in the atmosphere as secondary OC, when some volatile and semi-volatile organic compounds (VOC and SVOCS) are chemically transformed and the products undergo condensation or nucleation.

Although many recent researches have studied the carbonaceous fraction of PM, its chemical characterization is not comprehensively accomplished yet and some formation mechanisms are still unclear (Jacobson et al., 2000). In addition, the quantification of primary and secondary OC is a

very challenging task due to several reasons, such as the breaking down process of OC into primary and secondary organic carbon, potential sampling and analytical artefacts, effects of meteorological conditions during the sampling, etc. However, an estimation is possible through several indirect methods. Among others, the EC-tracer method is a widely accepted technique (Turpin and Huntzicker, 1995; Castro et al., 1999, Lim and Turpin 2002; Cabada et al., 2004; Harrison and Yin, 2008) and uses EC as a tracer of primary organic carbon (POC).

Several studies have been conducted across Italy on the carbonaceous PM (e.g., Lonati et al., 2005, 2007: Milan; Perrone et al., 2011: Milan; Larsen et al., 2012: Po Plain Italy; Cuccia et al., 2013: Milan; Malaguti et al. 2013: Trisaia ENEA Research Centre) and a recent review of available data was also recently published (Sandrini et al., 2014). However, data available for the Veneto Region, NE Italy, are quite limited so far. This is a serious gap, as Veneto is one of the most industrialized areas of Italy and is located in the Eastern part of the Po Valley, which is a well-known European hot-spot for many air pollutants, including PM₁₀, PM_{2.5} and PM₁₀-bound PAHs (Masiol et al., 2013). The presence of high mountain ranges, i.e. the Alps to the North and NW and the Apennines to the South, protects the Po Valley from cold winds coming from the NE (Larsen et al., 2012). In addition, the occurrence of frequent and prolonged wind calm periods, atmospheric stability conditions, persistent thermal inversions and lower planetary boundary layer heights during the night-time may favour the accumulation of locally-emitted pollutants especially during the coldest months (Masiol et al., 2014).

This study aims to (1) quantify the seasonal and spatial trends of carbonaceous aerosols in the Veneto Region; (2) investigate the effects of some meteorological factors on the carbonaceous PM variations, (3) estimate the contribution of secondary organic carbon (SOC) formation to the frequent exceeding of air quality standards for PM_{2.5} (4) investigate the potential local sources of carbonaceous PM_{2.5} in two cities selected as proxies for all the cities in the region because of their

differences in emission scenarios and geographic features, and (5) account for the potential effects of long-range transports on OC and EC levels.

2. MATERIALS AND METHODS

2.1. Study area

The Veneto Region has an area of $\sim 18.4 \cdot 10^3 \text{ km}^2$, extending for 210 km in the north-south and 195 km in the east-west directions. This region is characterized by a mountainous area (29%) at north, an intermediate hilly zone (15%) and a wide flat area located in the southern part. The morphological characteristics and climatic conditions have a decisive effect on the distribution of the population, which is mainly concentrated in the southern flat areas of the region, where there are several major cities and a continuum of minor urban centres. There are seven administrative provinces in Veneto: Belluno, Treviso, Vicenza, Venice, Padua, Verona and Rovigo.

2.2 Sample collection and analysis

A year-long sampling campaign (2012-2013) was conducted at 6 major cities located in 6 Provinces (Figure 1). Five cities (named Belluno (BL), Vicenza (VI), Venezia-Mestre (VE), Padua (PD) and Rovigo (RO)) are Province capitals, while the city of Conegliano (TV) was chosen for the Province of Treviso. Unfortunately, the Province of Verona was not included in this study. All sampling sites are operated by the Regional Environmental Protection Agency (ARPAV) and were chosen as representative of city-wide emissions. The characteristics of each station are given in Table 1.

The $\text{PM}_{2.5}$ samples were collected using low-volume samplers set according to the European standard EN 14907:2005, i.e. with a nominal flow of $2.3 \text{ m}^3 \text{ h}^{-1}$. Samples were collected on quartz fibre filters (47 mm \varnothing , Whatman QMA, GE Healthcare, USA) over 24 hours starting at midnight. As reported in EN 14907:2005, filters were conditioned for a period of at least 48 h before and after being weighted in a conditioning chamber equipped with a control system for constant temperature

and humidity (20 ± 1 °C and of $50\pm 5\%$ relative humidity) (Emerson S05KA Emerson Network Power – Piove di Sacco-Pd). An analytical balance (Sartorius series Genius, mod. SE2, Germany) with a sensitivity of 0.0001 mg was used to weight the PM mass (average of two measures). Samples were stored in clean Petri slides at a temperature of -20 °C to avoid sample degradation and losses of the more volatile compounds.

Sixty samples per site were selected for subsequent chemical analysis in every alternate month (April, June, August, October, December 2012 and February 2013): 10 samples per site in 10 consecutive days of the months selected. OC and EC concentrations were then determined on the selected filters by using a Sunset Lab OC-EC Aerosol Analyzer (Sunset Laboratory Inc., USA) and applying the NIOSH-5040 method. In brief, the speciation of OC and EC was achieved by placing a punch (1 to 1.5 cm²) of filter inside a quartz oven, where the sample is heated in four increasing temperature (ramps from 0 °C to 870 °C) in a completely oxygen free helium atmosphere in the first phase, and in a 2% oxygen/helium mixture atmosphere in the second phase. He-Ne laser light passing through the filter allows a continuous monitoring of filter transmittance, and thus the correction for the pyrolytically generated OC. Carbon evolved during both phases, is measured by a flame ionization detector (FID) after conversion to CH₄ inside methanator. Instrument calibration was achieved through injection of a known volume of methane into the sample oven for each analysis (Birch and Cary, 1996).

2.3 Quality control

Field blank samples were also collected in order to evaluate possible contaminations on OC concentrations. The calibration of the instrument was achieved by injecting on filter blanks four standards of increasing concentration of sucrose (Sigma Aldrich, purity $\geq 99\%$, ACS reagent). The limit of detection (LOD = 0.15 $\mu\text{g-C cm}^{-2}$) of OC was calculated as three times the standard

deviation of fields blanks and the coefficient of variation (<5%) was calculated by performing ten sample replicates for each calibration level.

2.4 Conditional probability function (CPF) and conditional bivariate probability function (CBPF)

Conditional probability function (CPF) is an important tool for the identification of local point sources (Kim et al., 2003; Kim et al., 2005) and it estimates the probability that a source is located within a particular wind direction sector, $\Delta\theta$ (Ashbaugh et al., 1985; Begum et al., 2010). CPF is defined as:

$$CPF_{\Delta\theta} = \frac{m_{\Delta\theta|c>x}}{n_{\Delta\theta}}$$

Where $m_{\Delta\theta}$ is the number of samples from the wind direction θ (22.5 degree in this study) having concentration C higher than or equal to a threshold value x and $n_{\Delta\theta}$ is the total number of samples of the same wind sector $\Delta\theta$. Here, x represents a high percentile concentration (75th or 90th).

Recently a new technique was developed by Uria-Tellaetxe and Carslaw (2014) combining conditional probability function with bivariate polar plots to detect and characterize the source of pollutants. Bivariate polar plots show how a concentration of a species varies jointly with wind speed and wind direction in polar coordinates and give directional information on sources as well as wind speed dependence of concentrations. The conditional bivariate probability function (CBPF) includes wind speed with CPF and allocates the observed pollutant concentration to a cell defined by ranges of wind direction and wind speed. It is defined as:

$$CBPF_{\Delta\theta,\Delta u} = \frac{m_{\Delta\theta,\Delta u | C>x}}{n_{\Delta\theta,\Delta u}}$$

Where $m_{\Delta\theta, \Delta u}$ is the number of samples from the wind direction $\Delta\theta$ with wind speed interval Δu having concentration C higher than or equal to a threshold value x and $n_{\Delta\theta, \Delta u}$ is the total number of samples in that wind direction-speed interval. Details of the CPF and CBPF methods can be found elsewhere (Uria-Tellaetxe and Carslaw, 2014). To estimate CPF and CBPF, daily measured OC, EC values were allocated to each hour of a given day to match hourly wind speed and wind direction data.

2.5 Back-trajectory analysis

A cluster analysis on the back-trajectories was performed to investigate the potential effects of long-range transports on the levels of OC, EC and TC. Back-trajectories were computed by using the HYSPLIT model (Draxler and Rolph, 2013; Rolph, 2013). The setup was: 96 h backward; starting height at 20 m a.s.l.; 4 trajectories per day at 3, 9, 15 and 21 UTC calculated separately for all the sites. A clustering algorithm using the Euclidean distance measure (Carslaw, 2014) was further applied to group back-trajectories into clusters depending on their potential origin.

3. RESULTS AND DISCUSSIONS

3.1 Overview on results

Summary statistics of the atmospheric concentrations of PM_{2.5}, Total Carbon (TC) and Total Carbonaceous Aerosols (TCA) at the stations representing the six provinces of Veneto region are listed in Table 2. PM_{2.5} concentrations varied from 3 to 83 $\mu\text{g m}^{-3}$ with a mean [mean \pm standard deviation (SD)] of 24 \pm 17 $\mu\text{g m}^{-3}$. The concentration of PM_{2.5} showed an increasing trend from warmer months (June, 12 $\mu\text{g m}^{-3}$, August, 17 $\mu\text{g m}^{-3}$) to colder months (December, 41 $\mu\text{g m}^{-3}$, February, 38 $\mu\text{g m}^{-3}$). The highest mean annual concentration was found in Padova (29 $\mu\text{g m}^{-3}$), followed by Vicenza (28 $\mu\text{g m}^{-3}$), Rovigo (27 $\mu\text{g m}^{-3}$) and Venice (25 $\mu\text{g m}^{-3}$), whereas comparatively lower mean concentrations were observed in Belluno (17 $\mu\text{g m}^{-3}$) and Treviso (18 $\mu\text{g m}^{-3}$). These PM levels are comparable to the concentrations normally observed in Milan (33 $\mu\text{g m}^{-3}$).

3, Lonati et al., 2005), ($58 \mu\text{g m}^{-3}$, winter, and $25 \mu\text{g m}^{-3}$, summer, Lonati et al., 2007) and Florence (annual mean value $19 \pm 10 \mu\text{g m}^{-3}$, Giannoni et al., 2012). Atmospheric dispersion due to increased wind speeds and wider mixing layer heights are recognised to be responsible for the lower PM concentrations in warmer months (Ferrero et al., 2010; Pecorari et al., 2013): while the typical planetary boundary layer height in the Po Valley is 450 m in winter (Bigi et al., 2012), it increases up to 1500-2000 m during summer due to thermal convective activity (Di Giuseppe et al., 2012).

The total organic mass associated with OC (here designated as organic matter, OM) was calculated by multiplying the measured OC by a factor of 1.4, as suggested by Lonati et al. (2005). TCA is calculated as sum of OM and EC. The average annual contribution of TCA to $\text{PM}_{2.5}$ is 37% ranging from 18% to 84%.

The mean OC concentration was $5.5 \pm 4 \mu\text{g m}^{-3}$ (mean \pm SD) accounting for 22% of the total $\text{PM}_{2.5}$ and 79% of the TC. On the contrary, EC varied from 0.2 to $11.9 \mu\text{g m}^{-3}$ with a mean value of $1.3 \mu\text{g m}^{-3}$ and contributed to 5% of the total $\text{PM}_{2.5}$ and 21% of the TC. A similar value was found by Lonati et al. (2007) in Milan, where the OC value ranged from 0.4 to $35.8 \mu\text{g m}^{-3}$ with a mean annual value of $9 \pm 7 \mu\text{g m}^{-3}$ and EC value ranged from 0.4 to $5 \mu\text{g m}^{-3}$ with mean annual value of $1.3 \mu\text{g m}^{-3}$. The concentrations of OC and EC reported in various European cities are given in Table 3.

3.2 OC/EC Ratio

The OC/EC ratios ranged from 0.7 to 15.4 with an annual mean value of 4.5 (Table 4). A similar result was observed in Milan (annual mean value 6.5) by Lonati et al. (2007) and at urban background (from 2.1 to 8.4) and urban traffic (from 2.9 to 8.3) sites in Tuscany (Giannoni et al., 2012). These values, which are similar to the values observed in most of the urban background sites in the Po Valley (summer: from 5 to 7; winter: from 3 to 10) and also comparable to the rural sites

of the Po Valley, suggest a regional influence of SOA coming from anthropogenic and biogenic sources in summer and the extensive wood burning utilization for residential heating in winter (Larsen et al., 2012). Condensations of gas phase semi-volatile organic species due to lower temperature combined with frequent events of air stagnation are responsible for increased OC/EC ratios in the Po Valley (Gilardoni et al., 2011; Larsen et al., 2012; Sandrini et al., 2014). However, the mean OC/EC ratios in this study were generally found above the values observed in most European cities. The OC/EC ratios in summer and winter in Amsterdam, Barcelona, and Ghent were 2.8-4.7, 2.6-3.1 and 3.5-4.4, respectively. The higher OC/EC ratios were referred to the formation of secondary organic carbon in addition to primary organic carbon (Kim et al., 2000; Na et al., 2004).

3.3 Spatial and seasonal trends

Monthly variations of OC and EC concentrations are shown in Figure 2. Generally the higher concentrations were found during colder months, while lower concentrations were found in the warmer ones. The highest OC level was observed in December ($11.4 \mu\text{g m}^{-3}$), the lowest in April ($2.2 \mu\text{g m}^{-3}$). The monthly organic carbon concentration gradually increased from April to December. Both the OC and EC concentrations were higher in February ($9.1 \mu\text{g m}^{-3}$), than in other months except December. Although the monthly mean of EC concentration does not exhibit larger variability, it follows the same pattern as OC with maxima during the colder months and minima in the warmer ones. Data categorized according to province, reveal the highest mean annual OC concentration in PD ($6.8 \mu\text{g m}^{-3}$), while the lowest mean value in TV ($4.5 \mu\text{g m}^{-3}$). OC concentrations varied slightly among the provinces and differences were not statistically significant as confirmed by a Kruskal–Wallis one-way analysis of variance (p -value 0.08). However, variations for EC values among the provinces were statistically significant (Kruskal–Wallis one-way analysis of variance test, p -value 0.00).

The combined effect of the lower air temperature favouring the particle-phase partitioning of semi-volatile organics and the additional emission sources in the form of biomass burning or household heating systems are possibly the main factors for higher OC concentrations in winter months (e.g., Viana et al., 2007; Schwarz et al., 2008). Moreover, the daily variability of OC concentrations is higher in winter than in summer, probably because of significant local contributions with remarkable daily variability, whereas homogenous contributions from regional-scale secondary organic aerosols are the reason behind lower variability of OC concentrations in summer months (Viana et al., 2007). The origin of carbonaceous aerosols can be evaluated from the relationship between OC and EC (Turpin and Huntzicker, 1995). A strong relationship between OC and EC is the indication of dominant primary sources (e.g. vehicle emissions, cooking, various combustion processes). In this study, a statistically significant positive correlation ($r=0.76$) between OC and EC was observed for all data in absence of any categorization. Before statistical analysis, normality of the data was tested and data of OC and EC were not normally distributed. This was confirmed by observing histograms, boxplots and finally by applying the Shapiro-Walk tests (assumption, $p < 0.05$ was not met). LogOC and logEC were used instead of OC and EC during statistical analysis as the normality assumption was not met and correlation analysis was performed using a robust procedure. The robust procedure description is provided as Supplementary Information (SI1).

By separating the data according to months, positive correlations between OC and EC were observed in all the months except December (Table 4). However, the correlation is comparatively higher in the warmer months than in the colder ones. This weaker correlation and higher OC/EC ratio during the winter months is probably due to the influence of SOC (Secondary Organic Carbon) formation or other significant primary organic sources (Na et al., 2004). This result is similar to the one obtained by Kim et al. (2000), who suggested that the OC and EC may not be emitted from a single dominant primary source (Na et al., 2004). The relationship between organic and elemental carbon for all provinces was also determined (Table 4).

An effort was made to compare the levels of carbonaceous particulate matter in weekdays and weekend (Figure SI2.1). Generally weekdays showed statistically significant higher EC and TC concentrations as compared to weekend, as confirmed by Mann-Whitney U test (p value = 0.000 for EC; p value = 0.02 for TC), whereas the differences between weekdays and weekend were not statistically significant for OC (p value = 0.069). All the measurement sites showed the same pattern: the highest TC concentration was on Wednesday, whereas the lowest one was observed on Sunday. This indicates nonappearance of pollution from commuting and other professional activities (Martellini et al., 2012). As the normality assumption ($p > 0.05$) was not met by Shapiro-Wilk test, a non-parametric Kruskal-Wallis one way analysis of variance was performed to test the significance of variations among days. Finally, a pair-wise comparison was carried out using the Wilcoxon rank sum test with Bonferroni correction and the results show that the TC levels of Wednesday are significantly different from those of Sunday (p value, 0.045). The highest OC concentrations were on Wednesday, whereas the highest EC concentrations on Thursday. Moreover, both OC and EC concentrations were higher on Saturday than on Monday, probably because most of the business operations are continuing on Saturday in Italy.

3.4 Factors affecting organic and elemental carbon levels

A correlation analysis between some weather parameters with organic and elemental carbon data was performed following a robust procedure in order to identify the factors affecting carbonaceous compounds variations (Table 5). OC and EC had a statistically significant negative relationship with temperature and solar radiation. This result suggests an increased emission during the winter months and it is similar to the findings of Li et al. (2012). OC and EC also showed a negative relationship with wind velocity. This is probably due to the clearing function of wind (Pindado et al., 2009). Similar results were also reported for PAHs measured across the Veneto region (Masiol

et al., 2013). A weak positive correlation was observed for both OC and EC concentrations with relative humidity. The absorption of pollutants may increase with the rises of humidity (Elbayoumi et al., 2013). For illustration purpose, data have been categorized into two groups to be consistent with the dates in which domestic heating is switched off (15 April) and on (15 October) according to the national legislation: warm period (from April to October 14) and cold period (from October 15 to March). The correlation of OC with temperature was positive in the warm period, negative in the cold one. A positive correlation between OC with temperature during the warm period may be due to the contribution of the secondary organic carbon (Grivas et al., 2004), whereas a negative correlation between OC and temperature may be related to the increased household heating during the cold period. An additional explanation for this negative correlation can also be found in the presence of lower pollutant dispersions with stable atmospheric condition during winter (Vardoulakis and Kassomenos, 2008). A negative correlation between wind velocity and organic and elemental carbon was observed in both the seasons.

Finally, statistically significant weather factors controlling OC and EC were investigated by fitting linear models using a robust procedure based on weighted likelihood (Markatou et al., 1998).

Robust techniques enable to overcome small deviations from normality and the presence of few outliers. A robust model selection procedure based on a weighted Akaike Information Criterion (Agostinelli, 2001) was also used, to choose the best model. This turned out to be the model including only temperature and wind. An additional confirmation was also provided by the robust t-test based on the full model in which temperature, humidity, wind velocity and solar radiation were considered as meteorological variables.

The selected model expression is the following:

$$\log(OC) = \alpha_1 \log(EC) + \alpha_2 \text{Temperature} + \alpha_3 \text{Wind} + \sum_{i=1}^6 \beta_i I(\text{Month}_i) + \varepsilon \dots\dots\dots (1)$$

A robust R^2 of the selected model is 0.79. The *p-value* and level of significance of the model parameters and other related information is provided as Supplementary Information (Table SI2.1, Figure SI2.2 and SI2.3). This procedure identifies three outliers, namely PD 39, 40 and VE 39 (see, SI2). After checking those observations, we found that comparatively higher relative humidity values were observed in these days and sampling sites (in PD, $RH > 91\%$ and VE, $RH > 95\%$). This may be one of the reasons.

3.5 Secondary organic Aerosol estimation

The quantification of primary and secondary organic carbon is quite difficult since no direct analytical methods are available. Several indirect methods have been used to estimate the secondary organic carbon. Among them, the EC tracer method is a widely accepted one: EC is used as a tracer of Primary Organic Carbon (POC) (Turpin and Huntzicker, 1995; Cabada et al., 2004). SOC is calculated by the following equation:

$$SOC = OC_{tot} - EC (OC/EC)_{pri} \dots\dots\dots(2)$$

Where OC_{sec} is the secondary OC and OC_{tot} is the measured total OC. Primary organic carbon (POC) is calculated from the EC $(OC/EC)_{pri}$. However, without conducting a complete profile of the organic carbon and emission source, it is difficult to define the contribution of the primary source. Several authors have recommended to substitute the minimum OC/EC ratio for the primary OC/EC (Castro et al., 1999):

$$SOC = OC_{tot} - EC (OC/EC)_{min} \dots\dots\dots(3)$$

Based on this approach, the minimum OC/EC ratio of this study is 1.29, which is the mean value of the lowest 5% OC/EC value. The mean annual primary and secondary organic carbon concentrations are $1.7 \mu\text{g m}^{-3}$ and $3.8 \mu\text{g m}^{-3}$, respectively (Table 6). In the cold period comparatively higher secondary organic carbon values were found than in the warm one. For illustration purpose, all data have been divided into two periods; warm period (April to October 14) and cold period (October 15 to March). The cold period mean SOC concentration is $6.8 \mu\text{g m}^{-3}$, contributing for 76% of the cold period TOC (Total Organic Carbon), while the warm period SOC ($1.4 \mu\text{g m}^{-3}$), contributes, on average, for 52% to the warm period TOC.

The EC/OC minimum ratio method and in general the EC tracer method have a limitation in the fact that they do not account for the variability of primary sources and do not consider non-combustion OC associated with EC, which is mainly of biogenic origin. A regression approach has been suggested to overcome this limitation (Turpin and Huntzicker, 1995):

$$SOC = OC - POC = OC - [aEC + b]$$

where a is the primary combustion ratio and b is the non-combustion primary OC. Basing on this approach, the annual mean of the SOC is $3.8 \mu\text{g m}^{-3}$, contributing for 69% of the total organic carbon; the warm period SOC is $1.3 \mu\text{g m}^{-3}$, contributing for 49% of the warm period OC and the cold period SOC is $6.4 \mu\text{g m}^{-3}$, contributing for 72% of the cold period OC (Table 6).

It is interesting to observe that SOC is higher in the cold period than in the warm one, differently from the expected pattern of higher concentration in the warm period as a consequence of favourable meteorological conditions and the occurrence of photochemical reactions. However, the seasonal variation of SOC follows the same trend of total OC with higher concentrations during the

household heating season, when higher emission of organic precursors occur. Moreover, a lower mixing layer height in winter favours SOC precursor stagnation and SOC formation (Dan et al., 2004; Duan et al., 2005). Under this view, a recent study carried out in VE by Pecorari et al. (2013) showed that the lower mixing height during winter and autumn tend to confine pollutants within 500 m of height. In summer, the mixing height reaches 1 km or more and therefore allows a greater dispersion of pollutants.

3.6 Conditional probability function (CPF) and conditional bivariate probability function (CBPF)

Among the six measurement sites, BL and VE have been selected to investigate the potential local sources of carbonaceous PM. BL is an interesting case of study for a number of reasons: (i) it is located in an alpine valley surrounded by high mountains, mostly peaking at ~800-2000 m; (ii) the atmospheric circulation is strongly affected by the arrangement of mountains; (iii) the sampling site is located in a public park in the middle of the city; (iv) both hardwood (from local trees) and softwood (mostly from conifers) are widely burned for domestic heating in stoves, most of which are dated, i.e. built with old technologies and without any system for emission mitigation; (v) road traffic is moderate; (vi) the site is located ~500 m East from a railway station, where trains are all diesel-powered; (vii) there are no large industries. On the contrary, VE has opposed characteristics: (i) it is located in a completely flat area; (ii) the wind regimes are affected by sea/land breezes in the warm seasons; (iii) the sampling site is located in the NE part of the city; (iv) methane is commonly used for domestic heating, but there has been a recent increase in the use of wood (i.e. logs, briquettes, chips and pellets) in modern stoves; (v) road traffic is intense with frequent congestion of the main roads in rush hours; (vi) a railway station is located ~2.6 km SSE (mostly electric-powered trains) and an international airport at ~6 km E; (vii) a large industrial area is hosted in the southern part of the city, including a main thermoelectrical power plant, oil refineries, incineration

facilities, chemical and steel plants. City maps with highlighted sources are reported as Figure SI2.4.

CPF plots for EC, OC concentrations and OC/EC ratios in BL and VE are provided in Figure SI2.5, whereas CBPF plots are shown in Figure 3. The plots for BL emphasize sectors, where the concentration is $>75^{\text{th}}$ percentile, equal to 1.5 and $6 \mu\text{g m}^{-3}$ for EC and OC, respectively. While CPF evidences that higher probabilities of high concentration may originate from all the directions, CBPF plots clearly show that the higher concentrations of EC and OC occur under wind calm conditions and for very low winds blowing from S (toward the historic city center). This wind regime corresponds to the prevailing wind direction in colder months, especially in December and February (Figure SI2.6) and indicates that domestic heating is the main source of both OC and EC. This result is also confirmed by analyzing the plot for OC/EC ratio. Both emission studies (e.g., Hildemann et al., 1991; Watson et al., 2001; Schauer et al., 2001; 2002) and monitoring campaigns at urban and rural sites (e.g, Schwartz et al., 2008; Harrison and Yin, 2008; de la Campa et al., 2009; Pirovano et al., 2015) reported larger proportion of OC emitted by biomass burning and domestic heating with respect to mobile sources. In particular, OC/EC ratios ranging from 1 to 4 have been reported for diesel- and gasoline-powered vehicles (Schauer et al., 2002), while OC/EC varying from 17 to 40 for wood combustion (Schauer et al., 2001). In BL, high probabilities of OC/EC >6.4 are evidenced toward the city centre, confirming the relative dominance of OC derived from biomass and wood burning. In the opposite way, despite mobile sources seem not to be the main sources of carbonaceous $\text{PM}_{2.5}$, their role as strong EC sources cannot be disregarded: the CBPF clearly shows that lower probabilities of high OC/EC ratios are measured to NE, i.e. toward a main traffic road often congested during weekends (most malls, shops and stores are to NE) and to WNW, i.e. toward main roads and the railway (diesel-powered trains only) and bus station.

CPF plots for VE indicate high probability of both EC and OC >75th percentile (i.e., 1.3 and 9.7 $\mu\text{g m}^{-3}$, respectively) for winds blowing from WSW and NW, while CBPF plots (Figure 3) show high probabilities mainly for winds blowing from WSW, i.e. toward the main urban area of Mestre, which also hosts some main roads affected by heavy traffic and an orbital road (Figure SI2.4). Some insights seem to point out that vehicular traffic is the main source of carbonaceous $\text{PM}_{2.5}$ in VE:

- The results are consistent with NO_2 data collected during 2000-2013 in the same site (Masiol et al., 2014). NO_2 is largely emitted by road traffic in urban environments and a recent increase in NO_2 levels in Europe has been related to the growing proportion of diesel-powered vehicles, which are known to have higher primary (direct) emissions of NO_2 (Carslaw et al., 2007);
- CBPF clearly shows that probabilities of high OC/EC ratios (>6.3) are measured mainly toward W and also spreading over the 1st and 2nd quadrant, i.e. toward the suburbs and semirural areas surrounding the city, where the use of alternative fuels to methane for domestic heating is increasing.

Finally it could be concluded that both biomass & wood burning and vehicular traffic are probably the main local sources of carbonaceous particulate matter in Veneto region.

3.7 Potential effects of long-range transports

In this study, four back-trajectories were simulated for each day and site in the flat areas of the region (VI, VE, PD and RO) as the topography of the territory may have effects on the reconstructions of back-trajectories for BL and TV, which are in and close to the Alps, respectively. The optimum number of clusters was then established by analyzing the change in the total spatial variance: all sites exhibited five main clusters with similar origins. Clusters (Figure 4) were then identified according to their provenance as: (1) Western Europe, (2) Mediterranean, (3) local, (4) Northern Europe and (5) Eastern Europe. The daily OC, EC and TC concentrations have been

subsequently assigned to each of the clustered trajectories. Statistics for chemical composition data in each cluster are presented in Table 7.

Generally, OC, EC and TC show similar results at all the sites, with concentrations slightly higher for clusters 1, 4 and 5 and the inter-cluster comparison shows only small differences. In particular, the site RO can be roughly selected as the most reliable one for analysing the long-range transports, as it is located far away from the mountain chains and the city has fewer local industrial emissions and traffic. In RO, the highest levels of OC are associated with air masses blowing from Northern ($6.7 \mu\text{g m}^{-3}$) and Eastern ($5.7 \mu\text{g m}^{-3}$) Europe, while results for the remaining origins are quite constant ($4\text{-}5 \mu\text{g m}^{-3}$). In summary, results indicate that trans-boundary transports have only a limited influence on the levels of OC and EC in the Veneto region.

4. CONCLUSIONS

In this work, for the first time, OC and EC concentrations were investigated in $\text{PM}_{2.5}$ in the Veneto region for an extended period of time. The mean organic carbon concentration was $5.48 \mu\text{g m}^{-3}$, contributing for almost 22% of the total $\text{PM}_{2.5}$ and 79% of the total carbon, while the mean EC value was $1.31 \mu\text{g m}^{-3}$, contributing for 5% of the total $\text{PM}_{2.5}$ and 21% to the total carbon. The monthly OC concentration gradually increased from April to December. The EC did not vary in accordance with OC, but the highest values were recorded in the colder months, as well. The OC/EC ratios ranged from 0.71 to 15.38 with a mean value of 4.54, which is higher than the values observed in most of the other European cities. In this study, a positive statistically significant relationship ($r=0.76$) between elemental and organic carbon was observed without any categorization of the data. However, the correlation is comparatively better in the warmer months than in the colder ones. A weak correlation coefficient between elemental and organic carbon during colder months suggests that the OC and EC may not be emitted from a single dominant primary source. Statistically significant micro-meteorological factors controlling organic and

elemental carbon were investigated by fitting linear models using a robust procedure based on weighted likelihood. Temperature and wind velocity turned out to be significantly related to the carbon fractions with a multiple R^2 value of 0.79. The secondary organic carbon contributed for 69% of the total organic carbon during the study period as confirmed by both the approaches of OC/EC minimum ratio and regression. It is interesting to observe that SOC is higher in the cold period than the warm one (in contrast with the expected pattern of higher concentration in summer), as a consequence of lower temperature and stable atmospheric conditions favouring accumulation of pollutants and hastening the condensation or nucleation of volatile organic compounds. The local contribution to OC and EC was investigated by using both CPF and CBPF. Plots indicate that both biomass & wood burning and vehicular emissions are probably the main local sources of carbonaceous particulate matter. The potential effects of long-range transports on the OC and EC levels were analysed by clustering the back-trajectories in the sites located in the flat areas of the region. Results revealed no significant differences in the levels of both OC and EC, when air masses had passed across different European regions, indicating that trans-boundary transports have a limited effect on the carbonaceous PM variations in the Veneto region.

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DISCLAIMER

This study was not financially supported by any public or private institution. The authors wish to state that the views expressed in this study are exclusively of their own and may not necessarily coincide with those of ARPAV.

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