FACTORS, ORIGIN AND SOURCES AFFECTING PM$_1$ CONCENTRATIONS AND COMPOSITION AT AN URBAN BACKGROUND SITE

Stefania Squizzato$^*$, Mauro Masiol$^{2,3}$, Chiara Agostini$^1$, Flavia Visin$^1$, Gianni Formenton$^4$, Roy M. Harrison$^{2,†}$, Giancarlo Rampazzo$^1$

$^1$Dipartimento di Scienze Ambientali, Informatica e Statistica, Università Ca’ Foscari Venezia, Campus scientifico, Via Torino 155, 30172 Mestre (VE), Italy
$^2$Division of Environmental Health and Risk Management School of Geography, Earth and Environmental Sciences University of Birmingham Edgbaston, Birmingham B15 2TT United Kingdom
$^3$Center for Air Resources Engineering and Science, Clarkson University, Box 5708, Potsdam, New York 13699, USA
$^4$Dipartimento Regionale Laboratori, Agenzia Regionale per la Prevenzione e Protezione Ambientale del Veneto (ARPAV), Via Lissa 6, 30174 Mestre (VE), Italy

ABSTRACT

$^*$ To whom correspondence should be addressed.
Tele: +39 041 234 8639, Email: stefania.squizzato@unive.it; stefania.squizzato81@gmail.com

$^†$ Also at: Department of Environmental Sciences / Center of Excellence in Environmental Studies, King Abdulaziz University, PO Box 80203, Jeddah, 21589, Saudi Arabia
PM$_1$ is widely believed to provide better information on the anthropogenic fraction of particulate matter pollution than PM$_{2.5}$. However, data on PM$_1$ are still limited in Europe as well as comprehensive information about its chemical composition and source apportionment and this gap is more evident in the pollution hot-spots still remaining in Europe, such as the Po Valley (Northern Italy). Elemental and organic carbon, 7 water soluble inorganic ions and 17 elements were quantified in 117 PM$_1$ samples collected at an urban background site in Venice-Mestre, a large city located in the eastern Po Valley, during winter (December 2013 – February 2014) and summer (May-July 2014) periods.

Results show a strong seasonality for PM$_1$ mass concentration (averages ranging from 6±2 in summer to 34±24 µg m$^{-3}$ in winter) and for most of the analyzed species. Components mainly related to road traffic, residential heating, biomass burning and secondary inorganic aerosol (ammonium nitrate) reached their highest levels in winter, while mineral dust and marine components were elevated in summer. PMF analysis revealed 7 potential sources. Secondary inorganic aerosol (33%) and biomass burning (33%) are the major contributor in winter followed by EC-primary emissions (16%), aged sulphate (6%), road traffic (7%), fossil fuel combustion (%) and marine aerosol (3%). During summer, these sources account for 12%, 14%, 20%, 22%, 8%, 14% and 10%, respectively.

Some PM$_1$ sources are located near the sampling site (residential area, traffic road, industrial area) but a major contribution of long range transport is observed when high pollution events occur. The results give useful insights into PM$_1$ composition in an urban area and chemical profiles of sources helpful in the interpretation of receptor model results.

**Keywords:** PM$_1$, water soluble inorganic ions, carbonaceous materials, mass closure, PMF

1. **INTRODUCTION**
In recent decades, the characterisation of airborne particulate matter (PM) has become an increasingly important topic of research since the epidemiological data have showed that PM has negative effects upon human health (Anderson et al., 2012; Rohr and Wyzga, 2012). Fine particles (with aerodynamic diameters of less than 2.5 μm, PM$_{2.5}$, and 1 μm, PM$_1$) may play an important role in affecting human health for a number of reasons: (i) they penetrate more effectively into the deep lung; (ii) they can penetrate more readily into indoor environments; (iii) they can remain suspended for longer periods of time in the atmosphere than coarse particles; (iv) they may be transported over long distances; (v) they tend to carry higher concentrations of the more toxic compounds, including acids, heavy metals and organic compounds and (vi) they have a larger surface area per unit mass compared to larger particles and, thus, can absorb larger amounts of semi-volatile compounds (e.g., Pope and Dockery, 2006). Consequently, the study of levels, composition and emission sources of fine particles in densely populated areas is very important for health protection and to improve PM control strategies.

Fine particles are typically mainly composed of elemental carbon (EC), organic carbon (OC), inorganic ions and metals. Among these major components, some studies have associated carbonaceous particles with health effects (Rohr and Wyzga 2012). These consist of compounds from combustion exhaust, soil, paved road dust, cooking and other sources (Harrison and Yin, 2008). EC comprises small (mainly sub-micrometre) graphitic particles which arise from primary emissions from combustion of various fuels, e.g., coal, wood, fuel oil and motor fuel, especially diesel. Organic carbon (OC) can be directly emitted into the atmosphere in the particulate phase or can originate in the atmosphere from gas-to-particle conversion processes (forming the so-called secondary organic aerosol, SOA) (Seinfeld and Pandis, 2006). Generally, EC lies in the submicrometre range, whereas OC exhibits wider size distributions (Pio et al., 2007).

Inorganic ions can be emitted from various primary sources, such as combustion, sea salt and crustal material. However, the main source of sulphate, nitrate and ammonium is the generation of
secondary inorganic aerosol (SIA) through (photo-) chemical reactions of gaseous precursors (NOx, SO2, NH3) and O3 with atmospheric oxidants to form mainly ammonium nitrate (NH4NO3) and ammonium sulphate ((NH4)2SO4)) (Seinfeld and Pandis, 2006).

Although metals generally represent a small fraction of PM1 mass, their contribution to the overall toxicity of particles cannot be disregarded. The chemical and physical properties of some elemental species is size-dependent: for example, the solubility of Pb, Co and Cd increase in fine particles, making those elements more bioavailable (Birmili et al., 2006). The characterisation of elemental composition is also very important for source apportionment studies: the variable proportion of some well known elemental markers can help in the identification of potential sources using receptor modelling techniques.

Although it has been suggested that PM1 can provide a better estimation of anthropogenic particles than PM2.5 (Perrone et al., 2013), PM1 source apportionment studies are still limited in Europe as well as comprehensive information about its composition (e.g. Perez et al., 2008; Vecchi et al., 2008; Theodosi et al., 2011; Perrone et al., 2013). Moreover, PM1 is not yet regulated in Europe and this is a major reason why there is a lack of available data and studies upon it. This is a serious gap, as some air pollution hotspots still remain in highly populated areas of Europe. Among others, the Po Valley (Northern Italy) deserves particular attention because of the frequent exceedance of guidelines and Limit Values fixed by EC Directives and international organizations such as WHO (Larsen et al., 2012). The present paper aims to investigate the composition of PM1 in Mestre-Venice, a large city on the eastern border of the Po Valley. Here, the highest concentrations of particulate matter and nitrogen oxides (NO+NO2=NOx) are commonly recorded in winter, while high levels of ozone are measured in summer due to photochemical processes involving precursors of natural and anthropogenic origin (Masiol et al., 2014a;b).
PM$_1$-bound elemental and organic carbon, water soluble inorganic ions and elements, have been analysed to determine the major contributors to PM$_1$ mass and were then processed to (i) determine the seasonal cycles, (ii) estimate secondary inorganic and organic aerosol, (iii) assess the major components applying a mass closure model, (iv) identify and quantify the most probable sources by using a receptor modelling technique (positive matrix factorization, PMF) and (v) hypothesize their location applying a conditional probability function.

2. MATERIAL AND METHODS

2.1 Measurement Site

Venice is located between the eastern edge of the Po Valley and the Adriatic Sea. Along with the city of Mestre, they form a large coastal urban municipality hosting 270,000 inhabitants (~ 628 inhabitants km$^{-2}$) (ISTAT, 2011). The local emission scenario includes some major potential sources of PM: high density residential areas; heavily trafficked roads mostly congested during peak hours; a motorway and a motorway-link which are part of the main European routes E55 and E70; an extended industrial area (Porto Marghera) and an international airport.

The sampling site (Via Lissa-Mestre, Lat. 45.4871 N –Long. 12.2229 E ) is located in a highly populated residential zone of Mestre surrounded by several heavily trafficked roads (distance ~ 450 m) (Fig. 1). The site was categorized as urban background by the local environmental agency (ARPAV). It lies about 200 m from an important motorway and few meters from the railway. Moreover, Via Lissa was chosen considering the background of information on PM$_{2.5}$ composition (Masiol et al., 2014b) that can help in the interpretation of PM$_1$ data.

2.2 Experimental

PM$_1$ samples were collected daily (117 samples) at an urban background site in Venice (Via Lissa-Mestre) during winter (December 2013 – February 2014) and summer (May-July 2014) periods.
using a low volume sampler (Skypost PM, Tecora, Milan) on quartz fiber filters. Sampling time was 24 h, from 0:00 to 24:00 and the flow rate was 2.3 m³ h⁻¹. PM₁ masses were measured by gravimetric determination (microbalance with 0.1 µg sensitivity) on filters preconditioned for 48 h at constant temperature (20°C) and relative humidity (50%).

Half of each sample was digested for elemental determination. Acid digestion was performed using 4 mL of 69% HNO₃, 1 mL H₂O₂ and 0.3 mL 48.9% HF in a microwave oven using the protocol proposed by Karthikeyan et al. (2006). An ICP-OES (Optima 5300 DV, Perkin Elmer) was used to determine the mass concentration of Mg, Al, S, K, Ca, Ti, Mn, Fe, Zn, Ba while an ICP-MS (Elan 6100, Perkin–Elmer) was used for V, Ni, Cu, As, Cd, Sb, Pb.

For the analysis of ion components an aliquot (16 mm Ø disc) was punched from the filter. Punches were extracted in vials with 10 mL MilliQ water (resistivity= 18.2 MΩ•cm at 25°C, Millipore) and sonicated for 50 min. Extracts were pre-filtered on microporous (0.45 µm) PTFE membranes and injected in two Metrohm (Switzerland) ion chromatographic systems with conductivity detectors to quantify the concentrations of three anions (Cl⁻, NO₃⁻, SO₄²⁻) and five cations (Na⁺, NH₄⁺, K⁺, Mg²⁺, Ca²⁺). The analytical ion chromatography method is reported elsewhere (Masiol et al., 2015a). Finally, an aliquot of filter (1 cm²) was analysed for elemental and organic carbon by using a Thermal–Optical Carbon Aerosol Analyser (Sunset Laboratory, Forest Grove, OR, USA) following the EUSAAR2 protocol (Table SI1). The carbon analyzer employs a programme of temperature and gas composition to evolve carbon species and a laser at a wavelength of 680 nm to monitor the filter transmittance (Birch and Cary, 1996).

Field blanks were prepared and analyzed together with the samples and the values obtained were routinely subtracted. Limits of detection (LODs) were calculated as three times the standard
deviation of field blanks (Table SI2): data below the LODs were substituted by LOD/2 for the statistical processing.

Gaseous pollutants data were provided by ARPAV (local environmental protection agency for Veneto region) whereas meteorological data refer to station 5 of the monitoring network of Ente Della Zona Industriale di Porto Marghera.

2.3 QA/QC and Uncertainties

The quality of the analytical procedures was checked by blank controls, by evaluating detection limits (DLs), recoveries, accuracy, and repeatability. The accuracies of quantitative analyses were assessed by analyzing certified liquid standards (TraceCERT, Fluka) for standard reference materials for elements (SRM 1648, NIST). OC and EC analyses were routinely checked by re-analysing sucrose calibration standards (relative standard deviation <4%). The recoveries of ions and elements were in the range of 80–110%. The relative standard deviation of each ion and elemental recoveries was < 5%.

2.4 PMF Settings

USEPA PMF 5.0 was used in this study. PMF was performed strictly following the main rules and suggestions found in the user manual (USEPA, 2014) and in Reff et al. (2007). Details of PMF settings and regression diagnostics are provided as supplementary materials (SI1 and Table SI3).

Data and uncertainties were handled according to Polissar et al. (1998): (1) data < DLs were set as DL/2, with an uncertainty of 5/6 of the corresponding DL; (2) data > DLs were matched with uncertainties determined by compounding errors from the most uncertain components with the addition of 1/3 of the DLs.
3. RESULTS AND DISCUSSION

3.1 Overview on PM$_1$ Levels and Composition

3.1.1 PM levels and main components

Table 1 summarizes the average seasonal concentrations of PM$_1$ and its components, gaseous pollutants and meteorological variables. The average PM$_1$ concentration over the whole period was 21±22 µg m$^{-3}$. PM$_1$ concentrations show the typical pattern of the study area, lower in warmer seasons and higher in the colder period (6.4±2.2 µg m$^{-3}$ and 34±24 µg m$^{-3}$ mean, respectively).

Measured levels are comparable with those observed by Perez et al. (2008) (19 µg m$^{-3}$ annual mean) at an urban background site in Barcelona (Spain) (5.8 µg m$^{-3}$, summer time) and with those previously detected in Venice by Valotto et al. (2014) (26.6 µg m$^{-3}$, winter time). Moreover, similar concentrations during winter were observed at other sites in Italy whereas summer concentrations in this study tend to be lower (Vecchi et al., 2004; Vecchi et al., 2008) but comparable with those observed in Birmingham (UK) (Harrison and Yin, 2008) (Table 2). This may be due to the higher wind speeds experienced in the summer period that tend to favour PM dispersion resulting in a drop of concentration. Furthermore in the study area PM$_1$ is strongly associated with mixed combustion processes dominating in winter including domestic heating (Valotto et al., 2014).

During winter the PM$_1$ fraction makes a major contribution to PM$_{10}$, averaging about 60% of PM$_{10}$ mass. On the contrary, the coarse fraction prevails in summer when the PM$_1$ contribution to PM$_{10}$ tends to be lower (40% on average). Similarly, PM$_1$ represents about 60% of PM$_{2.5}$ with the highest percentage in winter and the lowest in summer (67 and 43% of mean, respectively) (Table 2).

Chemical composition measurements of PM$_1$ showed that total carbon (TC) and secondary inorganic aerosol (SIA) represent the main components reaching 34% and 22% of the annual mean, respectively. During winter these components make up about 68% of PM$_1$, on the contrary during
the summer the elemental contribution increases and reaches 24%, whereas TC and SIA contribute
25% and 18% of PM$_1$ mass, respectively.

3.1.2 Water soluble inorganic ions

Ammonium, nitrate and sulphate contribute about 76 % of the total inorganic ionic species mass
(83% and 69% in winter and summer periods, respectively). As previously observed in PM$_{2.5}$
samples (Squizzato et al., 2013), sulphate dominates over nitrate in summer whereas in winter
nitrate dominates over sulphate. This behaviour can be explained by the semi-volatility of
ammonium nitrate. Other anions and cations contribute a minor fraction of the water-soluble
species (17 and 31% in winter and summer, respectively). All concentrations of Ca$^{++}$ were below
the detection limit.

Ammonium and sulphate are correlated both in the winter and summer periods (r=0.79 and r=0.78,
respectively). Nitrate, whose concentrations strongly depend on the meteorological conditions,
shows a strong correlation with both ammonium and sulphate during winter (r=0.97 and r=0.75,
respectively), but during summer the correlation with ammonium is lower (r=0.53) and practically
absent with sulphate (r=0.24).

As proposed by Cheng et al. (2011), a comparison between the calculated and observed $\text{NH}_4^+$
concentrations was conducted to evaluate the formation of secondary ions (Figure 2). The $\text{NH}_4^+$
concentration can be calculated based on the stoichiometric ratios of the major compounds (i.e.
ammonium sulphate [(NH$_4$)$_2$SO$_4$], ammonium bisulphate [NH$_4$HSO$_4$] and ammonium nitrate
[NH$_4$NO$_3$]); assuming that NO$_3^-$ is in the form of NH$_4$NO$_3$ and that SO$_4^{2-}$ is in the form of either
(NH$_4$)$_2$SO$_4$ or NH$_4$HSO$_4$. During winter, the slope is 0.98 when (NH$_4$)$_2$SO$_4$ is assumed and 0.88
when NH$_4$HSO$_4$ is assumed. This suggests that aerosol is fully neutralized by available ammonia.
Summer samples present different relationships: the slope was 2.86 and 1.70 assuming (NH$_4$)$_2$SO$_4$
and NH₄HSO₄, respectively. In this case, the aerosol may be acidic (i.e., not fully neutralized with available NH₄⁺) and mainly in the form of NH₄HSO₄. However, the pronounced scatter in the summer data in Figure 2 suggests that other forms of sulphates and nitrates may be present. Despite this, the anion/cation balance shows neutral conditions (Figure SI1) and no significant differences can be observed between winter and summer with slopes of 0.90 (r²=0.98) and 0.93 (r²=0.80), respectively.

Ammonium nitrate is a semi-volatile species and exists in reversible phase equilibrium with nitric acid in the gas phase. At higher temperatures and lower relative humidity, ammonium nitrate will evaporate. At temperatures exceeding 25°C (as in our summer conditions) evaporation is almost complete (Schaap et al., 2004) and this can lead to a deficiency of ammonium in the summer samples. The volatilised nitrate, in the form of nitric acid, can react with other cations. Na⁺ is the second most abundant cation presents in PM₁ samples; hence the relationship between sodium, nitrate and chloride (considering NaCl as the main form of sodium in the study area due to the proximity of the sea) was investigated by using a multiple regression analysis. During winter, Na⁺ is mainly present in the form of NaCl (Na⁺ = 0.31 +1.03[Cl⁻] - 0.47[NO₃⁻]; r²_adj=0.68), while during summer Na⁺ can also be present as NaNO₃ (Na⁺ = 0.93[Cl⁻] +0.15[NO₃⁻]; r²_adj=0.94), maintaining the neutral conditions previously observed.

### 3.1.3 Elements

On an annual basis nitrate, sulphate, ammonium, potassium and calcium represent the main inorganic components of PM₁. The Kruskal-Wallis test was applied to evaluate intra-seasonal differences. Among the analysed elements only Ti, Ba, Ni, Cd and Sb do not show a statistically significant seasonal difference (p>0.05). The others present a marked seasonal difference, with the higher concentration in winter, except for Ni and V.
Ni and V show the highest mean concentration during summer. This behaviour has been observed in a previous study (Masiol et al. (2014b); fossil fuel emissions (identified by Ni-V association) reached their highest levels in spring and summer in PM$_{2.5}$ and showed a significant drop in winter. These elements are strongly associated with combustion of fuel oil, and increased shipping traffic in the cruise harbour.

Sulphur is present mainly as sulphate in both the winter and summer period, and shows a higher average concentration in winter. Potassium is mainly present in the ionic form probably linked to wood combustion for residential heating (McDonald et al., 2000). Scatterplots between element and ionic form are provided as supplementary material (Figure SI2). Considering the uncertainties associated with low concentrations, LODs and concentration of total Ca and soluble Ca (Ca$^{++}$), it could be stated that almost all calcium is in insoluble form.

Average elemental concentrations have been computed for working days (from Monday to Friday) and week-end days (Saturday, Sunday and holidays) to highlight which elements are mainly associated with working cycles. The largest differences were observed in winter. Among the determined elements, Mn and Ni increase strongly during working days (Mn +105%; Ni +65%) and Ca, Mg, Zn and V show a slight enrichment (+27%, +15%, +26% and +22%, respectively). These elements are associated with road traffic emissions due to tyre wear, brake wear and resuspension (Pant and Harrison, 2013 and references therein). Moreover all these elements are often present predominantly in the finer fraction (<0.61 µm) and in intermediate fractions (0.61 -4.9 and 1 - 4 µm) (Fernandez Espinosa et al., 2001; Masiol et al., 2015b; Samara and Voutsa, 2005).

Compositional data have been compared with those observed at the same site for a previous PM$_{2.5}$ campaign (Masiol et al., 2014b) (Table 2). NO$_3^-$, Mn, Cu, V, Ni, As and Cd appear to be enriched in the finest fraction whereas Ti, Fe, S and Pb are mainly distributed in the PM$_{1.2.5}$ fraction. Table 2
also reports a comparison of PM elemental composition with other studies. Generally, higher concentrations have been observed for Ca, Mg, Al in our study. Other elements present comparable concentrations or are slightly lower than other studies.

3.1.4 Carbonaceous aerosol

Over the whole period OC ranged from 0.4 to 45.0 µg m\(^{-3}\) and EC ranged from 0.1 to 9.6 µg m\(^{-3}\). Both components show a marked seasonal pattern with the higher concentrations in winter and the lower in summer (Table 1). As EC is a primary pollutant, derived from ground-level combustion processes, this behaviour is expected due to less effective dispersion processes in the cold period. Measured concentrations are of the same order of those observed in other Italian cities and lower than those detected in Barcelona (Spain) and Birmingham (United Kingdom) (Table 2).

During winter EC is strongly correlated with carbon monoxide \((r=0.89)\) and NO\(_x\) \((r=0.85)\), and similarly OC shows a strong correlation with carbon monoxide \((r=0.93)\) and NO\(_x\) \((r=0.86)\). On the other hand, during summer both components present weaker correlations with CO and NO\(_x\) \((r_{EC,CO}=0.61, r_{OC,CO}=0.49; r_{EC,NOx}=0.53, r_{OC,NOx}=0.39)\). It is not clear if CO and NO\(_x\) are mainly associated with traffic or with domestic heating emissions in the study area. Considering the recently released emissions inventory (ISPRA, 2015), CO emissions are mainly due to non-industrial combustion plant (39% and the greatest part linked to emissions from residential plant), road transport (36%) and other mobile sources (21%). As regards NO\(_x\) emissions, 40% was attributed to road transport, 27% to other mobile sources and only 7% to non-industrial combustion plant. However, weak correlation of both EC and OC with primary gaseous pollutants during the summer period suggests that combustion processes for domestic heating could be the principal source of EC and primary OC in winter and the secondary organic component may dominate in summer.
In the literature, the ratio between organic carbon and elemental carbon may be a first indication of the nature of the aerosol, namely if they are primary (POC) or secondary (SOC) organic carbon. Ratios greater than 2.0 - 2.5 may indicate the presence of secondary, therefore “aged” aerosols (Turpin and Huntzinger, 1995; Bougiatiati et al., 2013). Organic carbon concentrations are expected to be higher in such aerosols because of secondary aerosol formation via condensation of lower-volatility organic compounds onto particles as a result of photochemical reactions and oxidation rendering the organic species less volatile and enabling their partition to the particulate phase (Donahue et al., 2006). On this basis, SOC concentrations might be expected to be higher in summer than in winter period arising from enhanced photochemical formation (Harrison and Yin, 2008), but the lower temperatures in winter favour partitioning into the condensed phase.

To better understand the relative amounts of POC and SOC, the EC-tracer method proposed by Castro et al. (1999) as used by Harrison and Yin (2008) have been applied to winter and summer data, separately to limit the influence of atmospheric conditions. In the EC-tracer method, EC is used as a tracer for POC. These methodologies aim to determine the primary OC-EC ratio by identifying the periods where ambient concentrations are dominated by primary emissions, with SOA simply appearing as an increase in the OC/EC ratio relative to that of the primary OC/EC ratio (Turpin and Huntzinger, 1991).

The approach proposed by Cabada et al. (2004) consists of three main steps, briefly: (i) removal from the original dataset of the points where rain causes significant changes to the OC/EC ratio; (ii) identify days characterised by high probability of SOA formation by using ozone concentrations, in this study SIA has been used as indicator of secondary formation processes and days with both a high SIA concentration and high OC/EC ratio have been removed; (iii) identify periods where combustion-related sources dominated by using CO concentration; days when the OC/EC ratio drops in correspondence with high CO concentration are used to estimate the primary OC/EC ratio.
Harrison and Yin (2008) propose to plot OC concentration as a function of EC, then the lower bound of the data points is generally taken to represent a constant mixture of EC with primary OC. Points lying above that minimum ratio line contain additional OC, which is interpreted as being secondary.

Assuming that OC primary can be defined by,

\[
[POC] = [OC/EC]_p * [EC] + b,
\]

the contribution of secondary OC can be estimated as

\[
[SOC] = [OC] – [POC],
\]

Where \([POC]\) is the primary organic aerosol concentration, \([OC/EC]_p\) is the ratio of OC to EC for the primary sources affecting the site of interest, and \(b\) is the non-combustion contribution to the primary OC and sampling artefact (Cabada et al., 2004 and references therein). In the method proposed by Harrison and Yin (2008) \(b\) has been set to zero.

Despite the OC/EC ratio presenting higher values during winter than in summer (3.1 and 1.6 means, respectively) indicating a greater contribution of secondary aerosol during the winter, the percentage contribution of SOC to total OC is higher in summer (54%) than in winter (39.5%) for both methods used (Table 3). This is in agreement with the enhanced photochemical formation due to the increase of solar radiation during summer.
In order to gain further insights, POC was compared with K$^+$ concentrations, considering soluble potassium as a marker of biomass burning and thus of primary emission from this combustion source. Similarly, SOC was compared with NO$_3^-$ and SO$_4^{2-}$ representing the secondary inorganic aerosol. During winter K$^+$ shows high correlations with calculated POC and SOC. On the other hand, during summer when wood combustion is less prevalent and the secondary inorganic aerosol formation is less favoured with respect to winter, the correlation is lower between K$^+$ and POC and absent between SOC, NO$_3^-$ and SO$_4^{2-}$ (Table 3).

### 3.2 Mass closure for PM$_1$

A mass closure model has been constructed by using previously developed conversion factors for PM$_{2.5}$. The conversion factors adopted are reported in Table 4. As such, PM reconstructed mass (RM) equation takes the following form:

$$\text{RM} = \text{Secondary inorganic ions} + \text{OM (Organic Matter)} + \text{EC} + \text{Mineral dust} + \text{Salts} + \text{Heavy elements} + \text{K}^+$$

On the basis of previous observed relationships, some specific conversion factors have been applied to summer data: sulphate has been considered as NH$_4$HSO$_4$ and nitrate has been assumed as NH$_4$NO$_3$ and NaNO$_3$ according to the relation Na$^+$ = 0.93[Cl$^-$] + 0.15[NO$_3^-$].

Although the selected conversion factors have been usually applied to PM$_{10}$ and PM$_{2.5}$ data (Harrison et al., 2003; Chow et al., 2015), good results were obtained. A good model fit is demonstrated by three factors: high $r^2$, gradient close to 1.0 and a near-zero intercept (Yin and Harrison, 2008). According to these criteria, a very good mass closure fit was found in winter: high $r^2$ (0.96), gradient close to 1 (0.96) and near-zero intercept (0.17 µg m$^{-3}$). In summer, the mass closure fit can be considered good ($r^2 = 0.65$, gradient 1.39 and intercept -1.27 µg m$^{-3}$) indicating a
lower reconstructed mass than that measured. Results are consistent with those observed by Yin and Harrison (2008) on PM$_1$ samples. Regression equations are reported in Table 4 and the average composition of winter and summer samples appears in Fig. 3.

During winter OM and secondary components dominate the PM mass. On the other hand, in summer the major contributor to PM is mineral dust and the marine component (NaCl) increases linked to the sea-land wind regime that enhances the movement of air masses from the sea to the land during the daytime. When high pollution events occur (PM$_1$$>$50 µg m$^{-3}$, 17 days) no significant differences were observed in PM$_1$ composition, including a simultaneous increase of all components. Meteorological conditions can partially explain the enhanced concentration: a relatively lower temperature (7°C) and wind speed (1 m s$^{-1}$) with respect to the mean of the winter favour the condensation of secondary compounds and the accumulation of PM components. Furthermore, as observed for PM$_{2.5}$ samples (Squizzato et al., 2012), long range transport should contribute to the increase of PM concentrations.

### 3.3 PM$_1$ Sources

Seven factors were extracted from the PMF model. Modelled PM$_1$ mass concentrations successfully predicted PM$_1$ ($r^2 = 0.97$) and all scaled residuals were normally distributed. The source profiles obtained are given in Fig. 4 while time series and apportioned mass contributions on a seasonal basis are given in Fig. SI3. Results were interpreted on the basis of the presence of known tracers for the specific sources and considering seasonal variations:

- EC characterises the first extracted factor: this factor can represent the primary contribution to PM$_1$ considering EC as a marker of primary emissions from combustion processes (combustion of coal, fuel oil and motor fuel, especially diesel). Seasonally it contributes 6 and 2 µg m$^{-3}$ (16% and 20%) of PM$_1$ concentrations in winter and summer, respectively. Despite
the marked meteorological difference between winter and summer, the primary contribution appears to represent a rather invariant percentage of total mass.

- The second factor accounts for a large proportion of K\(^+\) and OC: this association well describes the biomass burning combustion source (Reche et al., 2012). The high percentage contribution to PM\(_1\) reached in winter (33\%) confirms this hypothesis. The close relationship between K\(^+\) and OC has been already been discussed in the previous section.

- Fe, Mn, Zn, Ni, Cu and Sb are the main markers of the third factor: they represent a mix of elements related to traffic as non-exhaust particle emissions. It has been shown that even with zero tail pipe emissions, traffic will continue to contribute to fine particles through non-exhaust emissions and it is estimated that nearly 90\% of the total emissions from road traffic will come from non-exhaust sources by the end of the decade. These elements arise from tyre wear, brake wear and resuspension (Pant and Harrison, 2013 and references therein). As with the EC primary emission, this source does not show a seasonal difference, contributing 7\% and 9\% of PM\(_1\) in winter and summer, respectively.

- The fourth factor explains more of 80\% of vanadium concentration and 40\% of cadmium: this association can represent a mixed contribution of fossil fuel combustion, petrochemical plant (V) and industrial activities such as steel production and zinc metallurgy (Cd) (Querol et al., 2007) probably related to the proximity (about 6 km) of the industrial area of Porto Marghera. Usually, V-Ni is the typical pair of elements indicative of fuel oil combustion, however Moreno et al. (2007) observed that this relationship is stronger in the coarse particles than in the fine particles. In this case, PMF is not able to split this factor into two different sources. This factor contributes to 3\% and 14\% of PM\(_1\) in winter and summer, respectively.

- The marine component is highlighted in the fifth factor (Na\(^+\), Cl\(^-\) and Mg): despite sea-salt particles being mainly distributed in the coarse fraction, some particles, are also present in the fine fraction. Marine contributions increase during summer (10\%, 1 µg m\(^{-3}\)) due to the sea-land breeze wind regime.
In the sixth factor, sulphate and Mg are associated: this factor is interpreted as aged sulphate due to the ageing of sea-salt aerosols i.e. to heterogeneous reactions with atmospheric S(VI), from the oxidation of S(IV) species. Similar to the previous factor, the highest contribution can be observed in summer (22%, 2 µg m⁻³) due to the advection of air masses from the Adriatic Sea and the Venice Lagoon.

The last factor represents the secondary inorganic component of PM₁: it links NH₄⁺, NO₃⁻ and SO₄²⁻ to a lesser extent. These secondary ions derive from gas-to-particle conversion processes involving (photo-) chemical reactions of gaseous precursors such as NOₓ, SO₂ and NH₃. The highest contribution is reached in winter (33%, 12 µg m⁻³) when the meteorological conditions (low temperature and high relative humidity) and the higher concentration of NOₓ tend to favour the formation and stability of ammonium nitrate.

In order to evaluate the possible location of each identified source and to confirm PMF results, CPF (conditional probability function) analysis has been applied to PMF source contributions. To minimize the effect of atmospheric dilution and seasonal behaviour, the daily fractional contributions from each source relative to the total of all sources were used rather than the absolute source contributions (Kim et al., 2003). The CPF estimates the probability that a given source contribution from a given wind direction will exceed a predetermined threshold criterion. CPF is defined as:

\[ CPF = \frac{m_{\Delta \theta}}{n_{\Delta \theta}} \]

where \( m_{\Delta \theta} \) is the number of occurrences from wind sector \( \Delta \theta \) (11.25 degree) that exceeded the threshold criterion, and \( n_{\Delta \theta} \) is the total number of data from the same wind sector. Calm winds (< 1 m s⁻¹) were excluded from this analysis due to the isotropic behaviour of the wind vane under calm winds. The threshold criterion has been fixed to the upper 25th percentile of the fractional
contribution of each source. The sources are likely to be located in the directions that have high
conditional probability values (Kim et al., 2005).

CPF values for each source that apportion to PM$_1$ are plotted in polar coordinates in Fig. 5. Lowest
directional probabilities are seen for biomass burning and secondary inorganic aerosol sources: this
should reflect a widespread pollution over the study area. Other sources show specific directions
associated with the highest probabilities. The highest probabilities for primary aerosol are reached
towards the north probably due to vehicle emission from the motorway link and urban traffic.

Road traffic shows high probabilities towards the north-west and south-east in correspondence with
a heavy trafficked road and railway close to the sampling site confirming that this source is mainly
associated with the resuspension of road dust rather than exhaust emissions.

Marine aerosol and aged sulphate show similar patterns with the highest probabilities towards the
south-east in correspondence with the Venice Lagoon and the Adriatic Sea about 5 km and 15 km
distant, respectively, supporting PMF source interpretation.

The high probabilities associated with fossil fuel combustion occur for wind blowing from the south
where the industrial area of Porto Marghera is located, confirming that this source should be related
to industrial activities.

4. CONCLUSIONS

PM$_1$ samples have been collected at an urban background site in Venice (Po Valley, Italy), within
one of the most polluted areas in Europe. The main components of PM were determined: water
soluble inorganic ions, elements, elemental and organic carbon. Collected data have been processed
to (i) determine seasonal behaviour, (ii) estimate secondary inorganic and organic aerosol, (iii)
estimate major components applying a mass closure model and (iv) identify and quantify most
probable sources by using positive matrix factorization (PMF) and hypothesize their location by using CPF. Therefore, the main findings can be summarized as follows:

- During the winter PM$_1$ fraction makes the highest contribution to PM$_1$ reaching about 60% of mass.
- Total carbon (TC) and secondary inorganic aerosol (SIA) represent the main components of PM$_1$ reaching 34% and 22% of the annual mean, respectively. During winter these components make up about 68% of PM; on the contrary during summer the elemental contribution increases and reaches 24%.
- Ammonium, nitrate and sulphate contribute about 76% of the total inorganic ionic species mass (83% and 69% in winter and summer period, respectively).
- On an annual basis nitrate, sulphate, potassium and calcium represent the main inorganic component of PM$_1$. Among the analysed elements only Ti, Ba, Ni, Cd and Sb do not show a statistically significant seasonal difference. The others present a marked seasonal difference, with the highest concentration in winter, except for Ni and V. This indicates that different processes and sources are involved in PM$_1$ formation and emission and these are strongly influenced by weather conditions.
- Over the whole period OC ranged from 0.4 to 45.0 µg m$^{-3}$ and EC ranged from 0.1 to 9.6 µg m$^{-3}$. Despite the OC/EC ratio presenting higher values during winter than in summer (3.1 and 1.6 µg m$^{-3}$ mean, respectively) indicating a greater contribution of secondary aerosol during the winter, the percentage contribution of SOC to total OC is higher in summer (54%) than in winter (39.5%). This is in agreement with enhanced photochemical formation due to the increase of solar radiation during summer, and exceeds the influence of lower temperatures upon partitioning of semi-volatiles.
- During winter OM and secondary components dominate the PM mass. On the contrary, in summer the major contributor to PM is mineral dust and increased marine components.
(NaCl). When highly polluted events occur (PM$_1 > 50$ µg m$^{-3}$, 17 days) no significant differences can be observed in PM$_1$ composition. Therefore, the increase in PM$_1$ concentration appears to be due to a simultaneous increase of all components.

- Seven PM$_1$ sources have been identified, among these biomass burning (33%) and secondary inorganic aerosol (33%) are the major contributors in winter, while in summer the aged sulphate contribution increases (22%) as well as fossil fuels (14%) and marine aerosol (10%) due to the decrease of the typical winter sources.

Although PM$_1$ is not regulated at European level, it could represent a better indicator of anthropogenic PM sources; in winter it represents the greatest part of PM$_{10}$ and PM$_{2.5}$.

**ACKNOWLEDGMENTS**

The authors would to thank Prof. E. Argese, L. Gobbo for the analytical support. Ente della Zona Industriale di Porto Marghera supplied weather data.

**DISCLAIMER**

The views expressed in this study are exclusively of the authors and may not reflect those of ARPAV.
REFERENCES


Vecchi, R., Marcazzan, G., Valli, G., Ceriani, M., Antoniazzi, C., 2004. The role of atmospheric dispersion in the seasonal variation of PM$_1$ and PM$_{2.5}$ concentration and composition in the urban area of Milan (Italy). Atmos. Environ. 38, 4437–4446.


Yin, J., Harrison, R. M., 2008. Pragmatic mass closure study for PM$_{1.0}$, PM$_{2.5}$ and PM$_{10}$ at roadside, urban background and rural sites. Atmos. Environ. 42, 980–988.
Figure 1. Study area and sampling site location (images from Google Earth).
Figure 2. Comparison between calculated and measured ammonium in PM1 (ammonium sulphate: calculated $\text{NH}_4^+ = 0.38 \times [\text{SO}_4^{2-}] + 0.29 \times [\text{NO}_3^-]$; ammonium bisulphate: calculated $\text{NH}_4^+ = 0.192 \times [\text{SO}_4^{2-}] + 0.29 \times [\text{NO}_3^-]$).
**Figure 3.** Comparison of mean composition of PM1 in winter, summer and during high pollution events (PM$_1 > 50$ µg m$^{-3}$).

**Figure 4.** Factor profiles obtained by PMF analysis.
Figure 5. CPF plots for the highest 25% of the mass contributions.
Table 1. Basic statistics of experimental values of PM$_{1}$, PM$_{10}$, organic and elemental carbon, inorganic ions, elements, gaseous pollutants and meteorological conditions for each season and whole sampling period. Analytical data refer to PM$_{1}$ fraction of particles.

<table>
<thead>
<tr>
<th></th>
<th>All</th>
<th>Winter$^{a}$</th>
<th>Summer$^{b}$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Valid N</td>
<td>Mean ± S.D.</td>
<td>Valid N</td>
</tr>
<tr>
<td>PM$_{1}$ µg m$^{-3}$</td>
<td>117</td>
<td>21±22</td>
<td>61</td>
</tr>
<tr>
<td>PM$_{10}$ µg m$^{-3}$</td>
<td>117</td>
<td>37±32</td>
<td>61</td>
</tr>
<tr>
<td>PM$<em>{1}$/PM$</em>{10}$ µg m$^{-3}$</td>
<td>117</td>
<td>0.5±0.2</td>
<td>61</td>
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<tr>
<td>OC µg m$^{-3}$</td>
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<td>7±9</td>
<td>61</td>
</tr>
<tr>
<td>EC µg m$^{-3}$</td>
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<td>61</td>
</tr>
<tr>
<td>OC/EC</td>
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<td>2.5±1</td>
<td>61</td>
</tr>
<tr>
<td>TC %</td>
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<td>34±14</td>
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</tr>
<tr>
<td>Na$^{+}$ µg m$^{-3}$</td>
<td>85</td>
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</tr>
<tr>
<td>NH$_{4}^{+}$ µg m$^{-3}$</td>
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<td>1±1.2</td>
<td>60</td>
</tr>
<tr>
<td>K$^{+}$ µg m$^{-3}$</td>
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<td>0.6±0.7</td>
<td>58</td>
</tr>
<tr>
<td>Mg$^{++}$ µg m$^{-3}$</td>
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<td>0.1±0.1</td>
<td>33</td>
</tr>
<tr>
<td>Cl$^{-}$ µg m$^{-3}$</td>
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<td>48</td>
</tr>
<tr>
<td>NO$_{3}^{-}$ µg m$^{-3}$</td>
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<td>2.8±3.4</td>
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</tr>
<tr>
<td>SO$_{4}^{2-}$ µg m$^{-3}$</td>
<td>116</td>
<td>1±0.8</td>
<td>61</td>
</tr>
<tr>
<td>SIA$^{c}$ %</td>
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<td>22±7</td>
<td>61</td>
</tr>
<tr>
<td>Ca ng m$^{-3}$</td>
<td>74</td>
<td>669±366</td>
<td>30</td>
</tr>
<tr>
<td>Mg ng m$^{-3}$</td>
<td>78</td>
<td>384±262</td>
<td>37</td>
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<tr>
<td>Al ng m$^{-3}$</td>
<td>79</td>
<td>327±243</td>
<td>32</td>
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<tr>
<td>Fe ng m$^{-3}$</td>
<td>49</td>
<td>81±103</td>
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<td>K ng m$^{-3}$</td>
<td>111</td>
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<tr>
<td>S ng m$^{-3}$</td>
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<td>487±336</td>
<td>57</td>
</tr>
<tr>
<td>Ti ng m$^{-3}$</td>
<td>95</td>
<td>2.4±1.2</td>
<td>48</td>
</tr>
<tr>
<td>Mn ng m$^{-3}$</td>
<td>113</td>
<td>5±12</td>
<td>57</td>
</tr>
<tr>
<td>Zn ng m$^{-3}$</td>
<td>101</td>
<td>28±30</td>
<td>60</td>
</tr>
<tr>
<td>Ba ng m$^{-3}$</td>
<td>39</td>
<td>10±30</td>
<td>4</td>
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<tr>
<td>As ng m$^{-3}$</td>
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<tr>
<td>Ni ng m$^{-3}$</td>
<td>67</td>
<td>2.5±1.9</td>
<td>42</td>
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<tr>
<td>Cu ng m$^{-3}$</td>
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<td>53</td>
</tr>
<tr>
<td>Cd ng m$^{-3}$</td>
<td>100</td>
<td>1.1±1.1</td>
<td>51</td>
</tr>
<tr>
<td>Pb ng m$^{-3}$</td>
<td>116</td>
<td>7±7</td>
<td>60</td>
</tr>
<tr>
<td>V ng m$^{-3}$</td>
<td>107</td>
<td>2.4±2.1</td>
<td>53</td>
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<tr>
<td>Sb ng m$^{-3}$</td>
<td>95</td>
<td>1.6±2.1</td>
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<td>Σelements$^{d}$ %</td>
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<td>13±17</td>
<td>61</td>
</tr>
<tr>
<td>Total accounted %</td>
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<td>76±15</td>
<td>61</td>
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<tr>
<td>CO mg m$^{-3}$</td>
<td>117</td>
<td>0.7±0.5</td>
<td>61</td>
</tr>
<tr>
<td>NO µg m$^{-3}$</td>
<td>117</td>
<td>37±53</td>
<td>61</td>
</tr>
<tr>
<td>NO$_{2}$ µg m$^{-3}$</td>
<td>117</td>
<td>34±12</td>
<td>61</td>
</tr>
<tr>
<td></td>
<td>µg m⁻³</td>
<td>117</td>
<td>90±92</td>
</tr>
<tr>
<td>----------------</td>
<td>--------</td>
<td>-----</td>
<td>-------</td>
</tr>
<tr>
<td>NOₓ</td>
<td>µg m⁻³</td>
<td>117</td>
<td>1.6±1.1</td>
</tr>
<tr>
<td>SO₂</td>
<td>W m⁻²</td>
<td>117</td>
<td>3270±2702</td>
</tr>
<tr>
<td>Solar radiation</td>
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</tr>
<tr>
<td>Relative humidity</td>
<td>%</td>
<td>117</td>
<td>82±13</td>
</tr>
<tr>
<td>Wind speed</td>
<td>m s⁻¹</td>
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<td>2.1±1</td>
</tr>
<tr>
<td>Rain</td>
<td>mm</td>
<td>117</td>
<td>345</td>
</tr>
</tbody>
</table>

Note:

- SIA (secondary inorganic aerosol) is expressed as sum of NH₄⁺, NO₃⁻ and SO₄²⁻.
- Ʃelements represents the sum of all elements except K and S which are included as K⁺ and SO₄²⁻.
- Solar radiation is presented as the mean of the daily total radiation during the reporting period.
- Rain is presented as the total precipitation during the reporting period.
Table 2. Comparison with previous studies available in the literature for similar sampling sites. PM, OC, EC and ions are in µg m\(^{-3}\), elements in ng m\(^{-3}\).

<table>
<thead>
<tr>
<th></th>
<th>This study</th>
<th>Valotto et al., 2014</th>
<th>Squizzato et al., 2013; Masiel et al., 2014b</th>
<th>Perez et al., 2008</th>
<th>Vecchi et al., 2004</th>
<th>Vecchi et al., 2008</th>
<th>Harrison and Yin, 2008</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Via Lissa (UB)</td>
<td>Marco Polo Airport (Venice)</td>
<td>Via Lissa (UB)</td>
<td>Barcelona (UB+traffic)</td>
<td>Milano (UB+traffic)</td>
<td>Milano (UB)</td>
<td>Firenze (UB)</td>
</tr>
<tr>
<td></td>
<td>Winter</td>
<td>Summer</td>
<td>Mean</td>
<td>Winter</td>
<td>Summer</td>
<td>Winter</td>
<td>Summer</td>
</tr>
<tr>
<td>PM(_{10})</td>
<td>56.9</td>
<td>16.3</td>
<td>37.5</td>
<td>45.2</td>
<td>19.3</td>
<td>51.0</td>
<td>15.0</td>
</tr>
<tr>
<td>PM(_{2.5})</td>
<td>51.0</td>
<td>14.0</td>
<td>26.6</td>
<td>34.5</td>
<td>24.3</td>
<td>4.0</td>
<td>2.0</td>
</tr>
<tr>
<td>PM1/PM(_{10})</td>
<td>0.6</td>
<td>0.4</td>
<td>0.5</td>
<td>0.6</td>
<td>0.3</td>
<td>0.5</td>
<td>1.1</td>
</tr>
<tr>
<td>OC</td>
<td>11.8</td>
<td>1.1</td>
<td>6.7</td>
<td>4.3</td>
<td>2.3</td>
<td>1.5</td>
<td>0.5</td>
</tr>
<tr>
<td>EC</td>
<td>3.5</td>
<td>0.6</td>
<td>2.1</td>
<td>1.8</td>
<td>1.4</td>
<td>1.2</td>
<td>0.8</td>
</tr>
<tr>
<td>OC/EC</td>
<td>3.4</td>
<td>1.9</td>
<td>2.7</td>
<td>2.4</td>
<td>1.9</td>
<td>1.5</td>
<td>0.7</td>
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<tr>
<td>NO(_3)</td>
<td>5.0</td>
<td>0.3</td>
<td>2.8</td>
<td>6.1</td>
<td>0.5</td>
<td>1.5</td>
<td>0.5</td>
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<tr>
<td>SO(_4)</td>
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<td>1.0</td>
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<td>2.7</td>
</tr>
<tr>
<td>NH(_4)</td>
<td>1.8</td>
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<td>1.0</td>
<td>3.3</td>
<td>1.0</td>
<td>1.2</td>
<td>1.0</td>
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<tr>
<td>SIA</td>
<td>8.0</td>
<td>1.2</td>
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<td>13.1</td>
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<td>1.9</td>
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<td>2.8</td>
<td>0.9</td>
<td>11.3</td>
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<tr>
<td>Zn</td>
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<td>10.7</td>
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<td>22.1</td>
<td>3.4</td>
<td>50.8</td>
<td>20.1</td>
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<td>Cu</td>
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<td>8.2</td>
<td>3.0</td>
<td>0.5</td>
<td>18.7</td>
<td>6.1</td>
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<tr>
<td>Ba</td>
<td>53.0</td>
<td>4.7</td>
<td>9.6</td>
<td>1.3</td>
<td>9.9</td>
<td>17.8</td>
<td>5.3</td>
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<tr>
<td>Fe</td>
<td>100.7</td>
<td>51.1</td>
<td>81.4</td>
<td>36.8</td>
<td>11.2</td>
<td>255.0</td>
<td>164.0</td>
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<tr>
<td>K</td>
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<td>967.0</td>
<td>134.0</td>
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<td>838.8</td>
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<td>354.0</td>
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<td>Mg</td>
<td>176.2</td>
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<td>37.5</td>
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<tr>
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<td>465.1</td>
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<td>97.0</td>
<td>220.0</td>
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<td>362.2</td>
<td>486.8</td>
<td>586.6</td>
<td>523.3</td>
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<td>V</td>
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<tr>
<td>Ni</td>
<td>1.9</td>
<td>3.5</td>
<td>2.5</td>
<td>1.7</td>
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<td>2.3</td>
<td>4.7</td>
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<td>15.0</td>
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<tr>
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<td>2.1</td>
<td>1.7</td>
<td>0.6</td>
<td>2.1</td>
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<tr>
<td>Cd</td>
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<td>1.1</td>
<td>1.1</td>
<td>0.7</td>
<td>0.3</td>
<td>1.3</td>
<td>1.3</td>
</tr>
</tbody>
</table>

UB: urban background site.
Table 3. Estimate of primary and secondary organic carbon (average concentrations) during winter and summer period and relationship with $K^+$, $NO_3^-$ and $SO_4^{2-}$.

<table>
<thead>
<tr>
<th>EC-tracer method</th>
<th>[OC/EC]p (µg m$^{-3}$)</th>
<th>Non-combustion primary OC, $b$ (µg m$^{-3}$)</th>
<th>$R^2$</th>
<th>SOC (µg m$^{-3}$)</th>
<th>POC (µg m$^{-3}$)</th>
<th>POC vs $K^+$</th>
<th>SOC vs $NO_3^-$</th>
<th>SOC vs $SO_4^{2-}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cabada et al. (2004)</td>
<td>Winter 1.87</td>
<td>0.173</td>
<td>0.92</td>
<td>5.4 (37%)</td>
<td>6.7</td>
<td>r=0.77</td>
<td>r=0.73</td>
<td>r=0.75</td>
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<tr>
<td></td>
<td>Summer 1.49</td>
<td>-0.0161</td>
<td>0.81</td>
<td>0.6 (55%)</td>
<td>0.9</td>
<td>r=0.58</td>
<td>r=-0.23</td>
<td>r=-0.14</td>
</tr>
<tr>
<td>Harrison and Yin (2008)</td>
<td>Winter 1.78</td>
<td>0.99</td>
<td>0.99</td>
<td>5.8 (42%)</td>
<td>6.2</td>
<td>r=0.77</td>
<td>r=0.74</td>
<td>r=0.76</td>
</tr>
<tr>
<td></td>
<td>Summer 1.04</td>
<td>0.93</td>
<td>0.93</td>
<td>0.6 (53%)</td>
<td>0.6</td>
<td>r=0.57</td>
<td>r=0.04</td>
<td>r=0.31</td>
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</tbody>
</table>
Table 4. Conversion factors used in mass closure and regression results ($y$, mass reconstructed using mass closure model and $x$, gravimetrically measured mass).

<table>
<thead>
<tr>
<th>Season</th>
<th>Secondary inorganic ions</th>
<th>Organic mass</th>
<th>Elemental carbon</th>
<th>Geological minerals/road dust</th>
<th>Salt</th>
<th>Trace elements</th>
<th>Others</th>
<th>Regression</th>
</tr>
</thead>
<tbody>
<tr>
<td>Winter ($n = 61$)</td>
<td>1.375 SO$_4^{2-}$ as (NH$_4$)$_2$SO$_4^a$</td>
<td>1.6 OC$^b$</td>
<td>1 EC$^c$</td>
<td>1.89Al+2.14Si+1.4Ca+</td>
<td>1.65Cl$^-$ as NaCl$^d$</td>
<td>1.25 Cu + 1.24 Zn + 1.08 Pb$^e$</td>
<td>K$^+$</td>
<td>$y = 0.96x + 0.17$</td>
</tr>
<tr>
<td></td>
<td>1.29 NO$_3^-$ as NH$_4$NO$_3^a$</td>
<td></td>
<td></td>
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</tr>
<tr>
<td>Summer ($n = 56$)</td>
<td>1.29 SO$_4^{2-}$ as NH$_4$HSO$_4^a$</td>
<td>1.6 OC$^b$</td>
<td>1 EC$^c$</td>
<td>1.89Al+2.14Si+1.4Ca+</td>
<td>1.65Cl$^-$ as NaCl$^d$</td>
<td>1.25 Cu + 1.24 Zn + 1.08 Pb$^e$</td>
<td>K$^+$</td>
<td>$y = 1.39x -1.27$</td>
</tr>
<tr>
<td></td>
<td>1.37*(0.15 NO$_3^-$) as NaNO$_3^a$</td>
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</tr>
</tbody>
</table>

$^a$ Harrison et al., 2003.
$^b$ Marcazzan et al., 2001.
$^c$ Chow et al., 2015 and references therein.
$^d$ Si concentration has been obtained from the Al/Si ratio (0.46); Fe* and K* indicate the part of iron and potassium concentration considered of crustal origin. As the first approximation: for Fe this fraction has been evaluated dividing the total concentration of this element for its EF$_{Al}$; for K this fraction has been calculated subtracting the K$^+$ to K total considering K$^+$ as a marker of biomass combustion.