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Factors, Origin and Sources Affecting PM1 Concentrations and Composition at an Urban Background Site

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DOI: 10.1016/j.atmosres.2016.06.002

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Document Version Peer reviewed version

Citation for published version (Harvard):

Squizzato, S, Masiol, M, Agostini, C, Visin, F, Formenton, G, Harrison, R & Rampazzo, G 2016, 'Factors, Origin and Sources Affecting PM1 Concentrations and Composition at an Urban Background Site', *Atmospheric Research*, vol. 180, pp. 262-273. https://doi.org/10.1016/j.atmosres.2016.06.002

Link to publication on Research at Birmingham portal

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2	FACTORS, ORIGIN AND SOURCES
3	AFFECTING PM₁ CONCENTRATIONS
4	AND COMPOSITION AT AN URBAN
5	BACKGROUND SITE
6	
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27	

28 ABSTRACT

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29 PM₁ is widely believed to provide better information on the anthropogenic fraction of particulate matter pollution than PM_{2.5}. However, data on PM₁ are still limited in Europe as well as 30 31 comprehensive information about its chemical composition and source apportionment and this gap 32 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 33 quantified in 117 PM₁ samples collected at an urban background site in Venice-Mestre, a large city 34 35 located in the eastern Po Valley, during winter (December 2013 - February 2014) and summer 36 (May-July 2014) periods.

37 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 38 39 related to road traffic, residential heating, biomass burning and secondary inorganic aerosol 40 (ammonium nitrate) reached their highest levels in winter, while mineral dust and marine 41 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 42 EC-primary emissions (16%), aged sulphate (6%), road traffic (7%), fossil fuel combustion (%) and 43 marine aerosol (3%). During summer, these sources account for 12%, 14%, 20%, 22%, 8%, 14% 44 and 10%, respectively. 45

Some PM₁ 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 PM₁ composition in an urban area and chemical profiles of sources
helpful in the interpretation of receptor model results.

50

51 Keywords: PM₁, water soluble inorganic ions, carbonaceous materials, mass closure, PMF

52

53 1. INTRODUCTION

54 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 55 56 negative effects upon human health (Anderson et al., 2012; Rohr and Wyzga, 2012). Fine particles 57 (with aerodynamic diameters of less than 2.5 µm, PM_{2.5}, and 1 µm, PM₁) may play an important 58 role in affecting human health for a number of reasons: (i) they penetrate more effectively into the 59 deep lung; (ii) they can penetrate more readily into indoor environments; (iii) they can remain 60 suspended for longer periods of time in the atmosphere than coarse particles; (iv) they may be 61 transported over long distances; (v) they tend to carry higher concentrations of the more toxic 62 compounds, including acids, heavy metals and organic compounds and (vi) they have a larger 63 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, 64 composition and emission sources of fine particles in densely populated areas is very important for 65 66 health protection and to improve PM control strategies.

67

68 Fine particles are typically mainly composed of elemental carbon (EC), organic carbon (OC), 69 inorganic ions and metals. Among these major components, some studies have associated 70 carbonaceous particles with health effects (Rohr and Wyzga 2012). These consist of compounds 71 from combustion exhaust, soil, paved road dust, cooking and other sources (Harrison and Yin, 72 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 73 74 diesel. Organic carbon (OC) can be directly emitted into the atmosphere in the particulate phase or 75 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 76 77 submicrometre range, whereas OC exhibits wider size distributions (Pio et al., 2007).

78 Inorganic ions can be emitted from various primary sources, such as combustion, sea salt and 79 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 (NO_x, SO₂, NH₃) and O₃ with atmospheric oxidants to form mainly ammonium nitrate (NH₄NO₃) and ammonium sulphate ((NH₄)₂SO₄)) (Seinfeld and Pandis, 2006).

83

Although metals generally represent a small fraction of PM_1 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.

91

92 Although it has been suggested that PM₁ can provide a better estimation of anthropogenic particles 93 than PM_{2.5} (Perrone et al., 2013), PM₁ source apportionment studies are still limited in Europe as 94 well as comprehensive information about its composition (e.g. Perez et al., 2008; Vecchi et al., 95 2008; Theodosi et al., 2011; Perrone et al., 2013). Moreover, PM₁ is not yet regulated in Europe and 96 this is a major reason why there is a lack of available data and studies upon it. This is a serious gap, 97 as some air pollution hotspots still remain in highly populated areas of Europe. Among others, the 98 Po Valley (Northern Italy) deserves particular attention because of the frequent exceedance of 99 guidelines and Limit Values fixed by EC Directives and international organizations such as WHO 100 (Larsen et al., 2012). The present paper aims to investigate the composition of PM₁ in Mestre-101 Venice, a large city on the eastern border of the Po Valley. Here, the highest concentrations of particulate matter and nitrogen oxides (NO+NO₂=NO_x) are commonly recorded in winter, while 102 103 high levels of ozone are measured in summer due to photochemical processes involving precursors 104 of natural and anthropogenic origin (Masiol et al., 2014a;b).

106 PM_1 -bound elemental and organic carbon, water soluble inorganic ions and elements, have been 107 analysed to determine the major contributors to PM_1 mass and were then processed to (i) determine 108 the seasonal cycles, (ii) estimate secondary inorganic and organic aerosol, (iii) assess the major 109 components applying a mass closure model, (iv) identify and quantify the most probable sources by 110 using a receptor modelling technique (positive matrix factorization, PMF) and (v) hypothesize their 111 location applying a conditional probability function.

112

113 **2.**

MATERIAL AND METHODS

114 **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.

121

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 PM₁ data.

128

129 2.2 Experimental

130 PM₁ samples were collected daily (117 samples) at an urban background site in Venice (Via Lissa-

131 Mestre) during winter (December 2013 – February 2014) and summer (May-July 2014) periods

132 using a low volume sampler (Skypost PM, Tecora, Milan) on quartz fiber filters. Sampling time

133 was 24 h, from 0:00 to 24:00 and the flow rate was 2.3 $\text{m}^3 \text{h}^{-1}$. PM₁ masses were measured by

134 gravimetric determination (microbalance with 0.1 µg sensitivity) on filters preconditioned for 48 h

135 at constant temperature (20° C) and relative humidity (50%).

136

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.

142

For the analysis of ion components an aliquot (16 mm Ø disc) was punched from the filter. Punches 143 144 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 145 injected in two Metrohm (Switzerland) ion chromatographic systems with conductivity detectors to 146 quantify the concentrations of three anions (Cl^- , NO_3^- , SO_4^{2-}) and five cations (Na^+ , NH_4^+ , K^+ , 147 Mg^{2+} , Ca^{2+}). The analytical ion chromatography method is reported elsewhere (Masiol et al., 148 2015a). Finally, an aliquot of filter (1 cm^2) was analysed for elemental and organic carbon by using 149 150 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 151 152 temperature and gas composition to evolve carbon species and a laser at a wavelength of 680 nm to 153 monitor the filter transmittance (Birch and Cary, 1996). 154 155 Field blanks were prepared and analyzed together with the samples and the values obtained were

156 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 thestatistical processing.

159

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.

163

164 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 reanalysing 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

- 171 elemental recoveries was < 5%.
- 172

173 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.

183 **3. RESULTS AND DISCUSSION**

184 **3.1** Overview on PM₁ Levels and Composition

185 **3.1.1 PM levels and main components**

186Table 1 summarizes the average seasonal concentrations of PM_1 and its components, gaseous187pollutants and meteorological variables. The average PM_1 concentration over the whole period was188 $21\pm22 \ \mu g \ m^{-3}$. PM1 concentrations show the typical pattern of the study area, lower in warmer189seasons and higher in the colder period ($6.4\pm2.2 \ \mu g \ m^{-3}$ and $34\pm24 \ \mu g \ m^{-3}$ mean, respectively).

190

Measured levels are comparable with those observed by Perez et al. (2008) (19 μ g m⁻³ annual mean) 191 at an urban background site in Barcelona (Spain) (5.8 μ g m⁻³, summer time) and with those 192 previously detected in Venice by Valotto et al. (2014) (26.6 µg m⁻³, winter time). Moreover, similar 193 194 concentrations during winter were observed at other sites in Italy whereas summer concentrations in 195 this study tend to be lower (Vecchi et al., 2004; Vecchi et al., 2008) but comparable with those 196 observed in Birmingham (UK) (Harrison and Yin, 2008) (Table 2). This may be due to the higher 197 wind speeds experienced in the summer period that tend to favour PM dispersion resulting in a drop 198 of concentration. Furthermore in the study area PM₁ is strongly associated with mixed combustion 199 processes dominating in winter including domestic heating (Valotto et al., 2014).

200

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).

205

206 Chemical composition measurements of PM₁ showed that total carbon (TC) and secondary

207 inorganic aerosol (SIA) represent the main components reaching 34% and 22% of the annual mean,

208 respectively. During winter these components make up about 68% of PM₁, on the contrary during

the summer the elemental contribution increases and reaches 24%, whereas TC and SIA contribute
25% and 18% of PM₁ mass, respectively.

211

212 **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.

220

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).

226

As proposed by Cheng et al. (2011), a comparison between the calculated and observed NH_4^+ 227 concentrations was conducted to evaluate the formation of secondary ions (Figure 2). The NH₄⁺ 228 229 concentration can be calculated based on the stoichiometric ratios of the major compounds (i.e. 230 ammonium sulphate $[(NH_4)_2SO_4]$, ammonium bisulphate $[NH_4HSO_4]$ and ammonium nitrate [NH₄NO₃]); assuming that NO₃⁻ is in the form of NH₄NO₃ and that SO₄²⁻ is in the form of either 231 232 (NH₄)₂SO₄ or NH₄HSO₄. During winter, the slope is 0.98 when (NH₄)₂SO₄ is assumed and 0.88 when NH₄HSO₄ is assumed. This suggests that aerosol is fully neutralized by available ammonia. 233 Summer samples present different relationships: the slope was 2.86 and 1.70 assuming (NH₄)₂SO₄ 234

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 (r^2 =0.98) and 0.93 (r^2 =0.80), respectively.

241

242 Ammonium nitrate is a semi-volatile species and exists in reversible phase equilibrium with nitric 243 acid in the gas phase. At higher temperatures and lower relative humidity, ammonium nitrate will 244 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 245 samples. The volatilised nitrate, in the form of nitric acid, can react with other cations. Na⁺ is the 246 247 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 248 proximity of the sea) was investigated by using a multiple regression analysis. During winter, Na⁺ is 249 mainly present in the form of NaCl (Na⁺= 0.31 + 1.03[Cl⁻] - 0.47[NO₃⁻]; $r^2_{adi}=0.68$), while during 250 summer Na⁺ can also be present as NaNO₃ (Na⁺= $0.93[Cl^-] + 0.15[NO_3^-]$; $r^2_{adi} = 0.94$), maintaining 251 252 the neutral conditions previously observed.

253 **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.

265

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.

272

Average elemental concentrations have been computed for working days (from Monday to Friday) 273 274 and week-end days (Saturday, Sunday and holidays) to highlight which elements are mainly 275 associated with working cycles. The largest differences were observed in winter. Among the 276 determined elements, Mn and Ni increase strongly during working days (Mn +105%; Ni +65%) and 277 Ca, Mg, Zn and V show a slight enrichment (+27%, +15%, +26% and +22%, respectively). These 278 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 279 280 predominantly in the finer fraction ($<0.61 \mu m$) and in intermediate fractions (0.61 - 4.9 and 1 - 4 281 μm) (Fernandez Espinosa et al., 2001; Masiol et al., 2015b; Samara and Voutsa, 2005).

282

283 Compositional data have been compared with those observed at the same site for a previous $PM_{2.5}$

284 campaign (Masiol et al., 2014b) (Table 2). NO₃⁻, 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 comparableconcentrations or are slightly lower than other studies.

- 289
- 290 **3.1.4 Carbonaceous aerosol**

Over the whole period OC ranged from 0.4 to $45.0 \ \mu g \ m^{-3}$ and EC ranged from 0.1 to $9.6 \ \mu g \ m^{-3}$. 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).

297

298 During winter EC is strongly correlated with carbon monoxide (r=0.89) and NO_x (r=0.85), and 299 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 300 301 ($r_{EC CO}=0.61$, $r_{OC CO}=0.49$; $r_{EC NOx}=0.53$, $r_{OC NOx}=0.39$). It is not clear if CO and NO_x are mainly 302 associated with traffic or with domestic heating emissions in the study area. Considering the 303 recently released emissions inventory (ISPRA, 2015), CO emissions are mainly due to non-304 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 305 306 attributed to road transport, 27% to other mobile sources and only 7% to non-industrial combustion 307 plant. However, weak correlation of both EC and OC with primary gaseous pollutants during the 308 summer period suggests that combustion processes for domestic heating could be the principal 309 source of EC and primary OC in winter and the secondary organic component may dominate in 310 summer.

312 In the literature, the ratio between organic carbon and elemental carbon may be a first indication of 313 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 314 315 (Turpin and Huntzinger, 1995; Bougiatiati et al., 2013). Organic carbon concentrations are expected 316 to be higher in such aerosols because of secondary aerosol formation via condensation of lower-317 volatility organic compounds onto particles as a result of photochemical reactions and oxidation 318 rendering the organic species less volatile and enabling their partition to the particulate phase 319 (Donahue et al., 2006). On this basis, SOC concentrations might be expected to be higher in 320 summer than in winter period arising from enhanced photochemical formation (Harrison and Yin, 321 2008), but the lower temperatures in winter favour partitioning into the condensed phase.

322

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).

330

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).

370

371 **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:

375

376 RM = Secondary inorganic ions + OM (Organic Matter) + EC + Mineral dust + Salts +

377 Heavy elements $+ K^+$

378

379 On the basis of previous observed relationships, some specific conversion factors have been applied 380 to summer data: sulphate has been considered as NH_4HSO_4 and nitrate has been assumed as 381 NH_4NO_3 and $NaNO_3$ according to the relation $Na^+=0.93[Cl^-]+0.15[NO_3^-]$.

382

383 Although the selected conversion factors have been usually applied to PM_{10} and $PM_{2.5}$ data

384 (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

388 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.

392

393 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 394 395 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 ($PM_1 > 50 \mu g m^{-3}$, 17 days) no significant 396 397 differences were observed in PM₁ composition, including a simultaneous increase of all 398 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 399 400 favour the condensation of secondary compounds and the accumulation of PM components. 401 Furthermore, as observed for PM_{2.5} samples (Squizzato et al., 2012), long range transport should 402 contribute to the increase of PM concentrations.

403

404 **3.3 PM**₁ **Sources**

405 Seven factors were extracted from the PMF model. Modelled PM_1 mass concentrations successfully 406 predicted PM_1 ($r^2 = 0.97$) and all scaled residuals were normally distributed.

407 The source profiles obtained are given in Fig. 4 while time series and apportioned mass

408 contributions on a seasonal basis are given in Fig. SI3. Results were interpreted on the basis of the
 409 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

411 PM₁ considering EC as a marker of primary emissions from combustion processes

412 (combustion of coal, fuel oil and motor fuel, especially diesel). Seasonally it contributes 6 and

413 $2 \mu g m^{-3}$ (16% and 20%) of PM₁ concentrations in winter and summer, respectively. Despite

the marked meteorological difference between winter and summer, the primary contributionappears 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 PM₁ 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 420 421 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-422 exhaust emissions and it is estimated that nearly 90% of the total emissions from road traffic 423 424 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 425 426 the EC primary emission, this source does not show a seasonal difference, contributing 7% 427 and 9% of PM₁ 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.,
- 431 2007) probably related to the proximity (about 6 km) of the industrial area of Porto Marghera.

432 Usually, V-Ni is the typical pair of elements indicative of fuel oil combustion, however

433 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.

435 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

437 particles being mainly distributed in the coarse fraction, some particles, are also present in the

438 fine fraction. Marine contributions increase during summer $(10\%, 1 \mu g m^{-3})$ due to the sea-

439 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

447 processes involving (photo-) chemical reactions of gaseous precursors such as NO_x , SO_2 and

448 NH₃. The highest contribution is reached in winter $(33\%, 12 \,\mu g \,m^{-3})$ when the meteorological

449 conditions (low temperature and high relative humidity) and the higher concentration of NO_x

450 tend to favour the formation and stability of ammonium nitrate.

451

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 464 contribution of each source. The sources are likely to be located in the directions that have high465 conditional probability values (Kim et al., 2005).

466

467	CPF values for each source that apportion to PM_1 are plotted in polar coordinates in Fig. 5. Lowest
468	directional probabilities are seen for biomass burning and secondary inorganic aerosol sources: this
469	should reflect a widespread pollution over the study area. Other sources show specific directions
470	associated with the highest probabilities. The highest probabilities for primary aerosol are reached
471	towards the north probably due to vehicle emission from the motorway link and urban traffic.
472	
473	Road traffic shows high probabilities towards the north-west and south-east in correspondence with
474	a heavy trafficked road and railway close to the sampling site confirming that this source is mainly
475	associated with the resuspension of road dust rather than exhaust emissions.
476	
477	Marine aerosol and aged sulphate show similar patterns with the highest probabilities towards the
478	south-east in correspondence with the Venice Lagoon and the Adriatic Sea about 5 km and 15 km
479	distant, respectively, supporting PMF source interpretation.
480	
481	The high probabilities associated with fossil fuel combustion occur for wind blowing from the south
482	where the industrial area of Porto Marghera is located, confirming that this source should be related
483	to industrial activities.
484	4. CONCLUSIONS
485	PM ₁ samples have been collected at an urban background site in Venice (Po Valley, Italy), within

485 FMT samples have been conected at an urban background site in Venice (Fo Vaney, hary), within 486 one of the most polluted areas in Europe. The main components of PM were determined: water 487 soluble inorganic ions, elements, elemental and organic carbon. Collected data have been processed 488 to (i) determine seasonal behaviour, (ii) estimate secondary inorganic and organic aerosol, (iii) 489 estimate major components applying a mass closure model and (iv) identify and quantify most

490 probable sources by using positive matrix factorization (PMF) and hypothesize their location by

491 using CPF. Therefore, the main findings can be summarized as follows:

- 492 During the winter PM₁ fraction makes the highest contribution to PM₁ reaching about 60%
 493 of mass.
- Total carbon (TC) and secondary inorganic aerosol (SIA) represent the main components of
 PM₁ 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 PM₁. 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 PM₁ 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

515	(NaCl). When highly polluted events occur ($PM_1 > 50 \ \mu g \ m^{-3}$, 17 days) no significant
516	differences can be observed in PM_1 composition. Therefore, the increase in PM_1
517	concentration appears to be due to a simultaneous increase of all components.
518	• Seven PM_1 sources have been identified, among these biomass burning (33%) and
519	secondary inorganic aerosol (33%) are the major contributors in winter, while in summer the
520	aged sulphate contribution increases (22%) as well as fossil fuels (14%) and marine aerosol
521	(10%) due to the decrease of the typical winter sources.
522	
523	Although PM_1 is not regulated at European level, it could represent a better indicator of
524	anthropogenic PM sources; in winter it represents the greatest part of PM_{10} and $PM_{2.5}$.
525	
526	ACKNOWLEDGMENTS
527	The authors would to thank Prof. E. Argese, L. Gobbo for the analytical support. Ente della Zona
528	Industriale di Porto Marghera supplied weather data.
529	
530	DISCLAIMER
531	The views expressed in this study are exclusively of the authors and may not reflect those of
532	ARPAV.
533	
534	

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719 720 Figure 1.

Study area and sampling site location (images from Google Earth). Venice ITALY oling Si Mestre Industrial area

Venice

Adriatic Sea

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Comparison between calculated and measured ammonium in PM_1 (ammonium sulphate: calculated $NH_4^+ = 0.38* [SO_4^{2-}] + 0.29*[NO_3^-]$; ammonium bisulphate: calculated $NH_4^+ = 0.192* [SO_4^{2-}] + 0.29*[NO_3^-]$). Figure 2.



747Figure 3.Comparison of mean composition of PM1 in winter, summer and during high748pollution events ($PM_1 > 50 \ \mu g \ m^{-3}$).

749





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 PM₁, PM₁₀, organic and elemental carbon,

inorganic ions, elements, gaseous pollutants and meteorological conditions for each season and

whole sampling period. Analytical data refer to PM₁ fraction of particles.

All Winter^a Summer^b Valid N Mean \pm S.D. Valid N Mean \pm S.D. Valid N Mean \pm S.D. $\mu g m^{-3}$ PM_1 21±22 34±24 117 61 56 6.4 ± 2 $\mu g m^{-3}$ PM_{10} 117 37 ± 32 61 57±33 56 16±7 PM_{1}/PM_{10} $\mu g m^{-3}$ 61 117 0.5 ± 0.2 0.6 ± 0.1 56 0.4 ± 0.1 $\mu g m^{-3}$ OC 117 7±9 61 11.6 ± 10 56 1.1±1 EC $\mu g m^{-3}$ 117 2.1 ± 2.2 61 3.5 ± 2.2 56 0.6 ± 1 OC/EC 117 2.5 ± 1 61 3.1±1 56 $1.6{\pm}1$ TC 117 34 ± 14 61 42.5±11.5 25±10 % 56 Na^+ $\mu g m^{-3}$ 85 0.5 ± 0.3 37 0.7 ± 0.3 48 0.4 ± 0.3 NH_4^+ $\mu g m^{-3}$ 1±1.2 1.8 ± 1 0.3±0.1 115 60 55 \mathbf{K}^+ $\mu g m^{-3}$ 75 0.6 ± 0.7 58 0.8 ± 1 17 0.1 ± 0.1 Mg^{++} $\mu g m^{-3}$ 0.1±0 7 0.1 ± 0.1 40 0.1 ± 0.1 33 Cl^{-} $\mu g m^{-3}$ 79 0.7 ± 0.5 48 0.8 ± 1 31 0.6 ± 0.4 NO_3^{-} $\mu g m^{-3}$ 2.8 ± 3.4 61 5±3 56 0.3±0.2 117 SO_{4}^{2} µg m⁻³ 116 1 ± 0.8 61 $1.4{\pm}1$ 55 0.6 ± 0.4 SIA^c % 117 22±7 61 25.3±7 56 18 ± 4 ng m⁻³ Ca 74 669±366 30 421±203 44 839±357 ng m⁻³ 78 384±262 37 176±140 41 572±196 Mg Al ng m⁻³ 79 327±243 32 124 ± 62 47 465±222 Fe ng m⁻³ 49 81±103 30 101±114 19 51±76 Κ ng m⁻³ 111 457±611 59 772±699 52 99±59 S ng m⁻³ 110 487±336 57 603±396 53 362±192 Ti ng m⁻³ 95 2.4±1.2 48 2.2±1 47 2.5±1 ng m⁻³ 5±12 Mn 113 57 8.8 ± 16 56 $1.9{\pm}1$ Zn ng m⁻³ 101 28 ± 30 60 39.6 ± 34 41 10.7 ± 7 ng m⁻³ 39 10 ± 30 4 53±90.9 Ba 35 4.7±3 As ng m⁻³ 110 1.2 ± 1.3 59 1.5 ± 2 51 0.8 ± 1 Ni ng m⁻³ 2.5±1.9 42 1.9 ± 2 25 3.5±1 67 ng m⁻³ Cu 89 8±25 53 12.7±32 36 1.6±1 $\mathbf{C}\mathbf{d}$ ng m⁻³ 100 1.1 ± 1.1 51 1.2 ± 1 49 1.1±1 Pb ng m⁻³ 116 7±7 60 10.5 ± 8 56 3.2±2 V ng m⁻³ 107 2.4±2.1 53 1.9±2 54 2.8±2 Sb ng m⁻³ 95 44 2.5±3 51 0.9±1 1.6 ± 2.1 Σ elements^d % 117 13±17 61 2.5 ± 3 56 24 ± 18 Total accounted % 76±15 61 75±9 76±20 117 56 mg m⁻³ CO 117 0.7 ± 0.5 61 $1.0{\pm}0.5$ 56 0.3±0.1 $\mu g m^{-3}$ NO 117 37±53 61 68±59 56 4 ± 4 NO_2 µg m⁻³ 117 34±12 61 40±12 56 26±6

NO _x	μg m ⁻³	117	90±92	61	143 ± 100	56	32±10
SO_2	μg m ⁻³	117	117 1.6±1.1		$1.4{\pm}0.9$	56	$1.7{\pm}1$
Solar radiation ^e	$W m^{-2}$	117	3270±2702	61	828±461	56	5930±1159
Temperature	°C	117	15±7	61	8±2	56	22±3
Relative humidity	%	117	82±13	61	93±6	56	71±9
Wind speed	$m s^{-1}$	117	2.1±1	61	$1.7{\pm}1$	56	2.6±1
Rain ^f	mm	117	345	61	248	56	98

^aWinter: December 7, 2013 – February 5, 2014.

^bSummer: May 7, 2014 – July 1, 2014.

^cSIA (secondary inorganic aerosol) is expressed as sum of NH_4^+ , NO_3^- and SO_4^{-2-} . ^d Σ elements represents the sum of all elements except K and S which are included as K⁺ and SO_4^{-2-} .

^eSolar radiation is presented as the mean of the daily total radiation during the reporting period.

774 775 ^fRain is presented as the total precipitation during the reporting period.

	,	This study		Valotto	et al., 2014	Squizzato Masiol et	et al., 2013; t al., 2014b	Perez et al., 2008	Vecchi	et al., 2004			Vecchi	et al., 2008			Harrison a	and Yin, 2008
	Via Lissa (UB)		B)	Marco F (V	Polo Airport 'enice)	lo Airport Via Lissa (UB) Barcelona Mi nice) (UB+traffic)		Milano (Milano (UB+traffic) Milano (UB)		Firenze (UB)		Genova (UB)		Birmingham (UB)			
	Winter	Summer	Mean	Winter	Summer	Winter	Summer	Mean	Winter	Summer	Winter	Summer	Winter	Summer	Winter	Summer	Winter	Summer
PM ₁₀	56.9	16.3	37.5	45.2	19.3													
PM _{2.5}						51.0	15.0											
PM1	34.3	6.4	20.9	26.6	5.8			19	41.0	16.4	48.8	19.4	25.3	11.8	11.5	17.4	12.6	9.2
PM_1/PM_{10}	0.6	0.4	0.5	0.6	0.3													
OC	11.8	1.1	6.7					4.3	17.8	6.1	14.80	4.80	12.00	2.70	5.00	3.40	2.8	2
EC	3.5	0.6	2.1					1.8	2.3	1.3	1.80	1.10	0.90	0.60	0.90	0.90	1.8	0.9
OC/EC	3.4	1.9	2.7					2.4	7.6	4.7	8.2	4.4	13.3	4.5	5.6	3.8		
NO_3^-	5.0	0.3	2.8			6.1	0.5	1.5			13.6	0.9	3.2	0.1	1.1	0.2	1.8	0.4
SO_4^{2-}	1.4	0.6	1.0			3.8	2.7	3.3			4.7	3.9	1.7	3.2	1.7	3.8	1.3	2.0
$\mathrm{NH_4}^+$	1.8	0.3	1.0			3.3	1.0	1.2			4.2	1.8	1.6	1.3	1	1.4		
SIA	8.0	1.2	4.6			13.1	4.0	6			22.5	6.6	6.5	4.6	3.8	5.4		
Ti	2.2	2.5	2.4	2.7	9.9	5.7	15.4	1.8	7	4	4	4	4	4	4	4		
Mn	8.8	1.9	5.4	2.8	0.9	11.3	3.8	4	9	4	9	5	2	2	1	3		
Zn	39.6	10.7	27.9	22.1	3.4	50.8	20.1	48	66	32	59	34	20	9	13	9		
Cu	12.7	1.6	8.2	3	0.5	18.7	6.1	12	7	3	7	4	4	4	2	7		
Ba	53.0	4.7	9.6	1.3	9.9	17.8	5.3	9										
Fe	100.7	51.1	81.4	36.8	11.2	255.0	164.0				86	42	41	26	24	37	100	20
Κ	771.9	98.8	456.6	528.5	31.4	967.0	134.0		257	81	300	98	270	94	91	59		
Ca	420.6	838.8	669.3	60	297.3	211.0	354.0		24	17	27	22	28	34	18	56	40	50
Mg	176.2	572.1	384.3	34.7	37.5	115.0	73.0											
Al	124.4	465.1	327.1	19.6	9.3	97.0	220.0		16	14	16	11	12	19	14	16		
S	602.7	362.2	486.8	586.6	523.3	1267.0	1340.0		1297	1445	1200	1500	560	1100	550	1000		
V	1.9	2.8	2.4	8	8.5	2.4	5.4	6	5	4	4	4	3	4	4	15		
Ni	1.9	3.5	2.5	1.7	0.6	2.3	4.7	3	7	2								
Pb	10.5	3.2	7.0			18.5	7.7	17	35	15								
As	1.5	0.8	1.2			2.1	1.7	0.6	2	1								
Cd	1.2	1.1	1.1	0.7	0.3	1.3	1.3	0.3										
UB: urba	n backg	round si	te.															

Table 2. Comparison with previous studies available in the literature for similar sampling sites. PM, OC, EC and ions are in μ g m⁻³, elements in ng m⁻³. 777

Table 3. Estimate of primary and secondary organic carbon (average concentrations) during winter and summer period and relationship with K^+ , NO₃⁻ and SO₄⁻². 781 782

EC-tracer method		[OC/EC]p	Non-combustion primary OC, b (µg m ⁻³)	R ²	SOC µg m ⁻³	POC µg m ⁻³	POC vs K ⁺	SOC vs NO ₃	SOC vs SO ₄ ²⁻
Cabada et al. (2004)	Winter	1.87	0.173	0.92	5.4 (37%)	6.7	r=0.77	r=0.73	r=0.75
	Summer	1.49	-0.0161	0.81	0.6 (55%)	0.9	r=0.58	r=-0.23	r=-0.14
Harrison and Yin (2008)	Winter	1.78		0.99	5.8 (42%)	6.2	r=0.77	r=0.74	r=0.76
	Summer	1.04		0.93	0.6 (53%)	0.6	r=0.57	r=0.04	r=0.31

784 **Table 4.** Conversion factors used in mass closure and regression results (y, mass reconstructed using mass closure model and x, gravimetrically

measured mass).

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Season	Secondary inorganic ions	Organic	Elemental	Geological minerals/road	Salt Trace elements		Others	Regression
		mass	carbon	dust				
Winter	$1.375 \text{ SO}_4^{2-} \text{ as } (\text{NH}_4)_2 \text{SO}_4^{-a}$	1.6 OC ^b	1 EC ^a	1.89Al+2.14Si+1.4Ca+	1.65Cl ⁻ as NaCl ^a	1.25 Cu + 1.24 Zn + 1.08 Pb ^c	\mathbf{K}^+	y = 0.96x + 0.17
(n = 61)	1.29 NO_3^- as $\text{NH}_4 \text{NO}_3^-$ a			1.43Fe*+1.67Ti+1.2K* ^{c,d}				
Summer	1.29 SO_4^{2-} as NH ₄ HSO ₄ ^a	1.6 OC ^b	1 EC ^a	1.89Al+2.14Si+1.4Ca+	1.65Cl ⁻ as NaCl ^a	1.25 Cu + 1.24 Zn + 1.08 Pb ^c	\mathbf{K}^+	y = 1.39x - 1.27
(n = 56)	1.29*(0.85 NO ₃ ⁻) as NH ₄ NO ₃ ^a			1.43Fe*+1.67Ti+1.2K* ^{c,d}				
	1.37*(0.15 NO ₃ ⁻) as NaNO ₃ ^a							

^a Harrison et al., 2003.

^b Marcazzan et al., 2001.

789 ^cChow et al., 2015 and references therein.

⁴Si 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

 $\frac{791}{792}$ 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.

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