

1 **Supplementary Material**

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5 **Inter-annual variability of source contributions to PM₁₀, PM_{2.5}, and oxidative potential in an**
6 **urban background site in central Mediterranean**

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Species ($\mu\text{g}/\text{m}^3$)	2016-2017 (124 samples)		2013-2014 (113 samples)	
	PM ₁₀	PM _{2.5}	PM ₁₀	PM _{2.5}
PM	26.9 (12.7)	18.0 (11.4)	29.5 (19.2)	18.7 (11.3)
EC	1.09 (1.03)	1.00 (0.95)	0.80 (0.65)	0.58 (0.42)
OC	5.45 (5.02)	4.70 (4.75)	5.72 (4.95)	5.05 (4.84)
K ⁺	0.30 (0.44)	0.23 (0.22)	0.32 (0.37)	0.27 (0.36)
Na ⁺	0.91 (0.83)	0.23 (0.27)	0.99 (0.89)	0.26 (0.22)
Cl ⁻	0.77 (0.85)	0.26 (0.13)	0.85 (1.40)	0.17 (0.21)
NH ₄ ⁺	0.42 (0.48)	0.40 (0.44)	0.88 (0.94)	0.87 (0.94)
SO ₄ ²⁻	2.41 (1.26)	2.13 (1.09)	3.05 (1.93)	2.61 (1.78)
NO ₃ ⁻	1.87 (1.94)	0.99 (1.22)	1.48 (1.51)	0.77 (1.15)
Mg ²⁺	0.15 (0.08)	0.06 (0.05)	0.19 (0.15)	0.03 (0.04)
Ca ²⁺	0.82 (0.71)	0.45 (0.47)	0.96 (0.92)	0.23 (0.25)
Al	0.27 (0.35)	0.17 (0.24)	0.23 (0.35)	0.16 (0.16)
Fe	0.27 (0.28)	0.09 (0.09)	0.24 (0.32)	0.09 (0.08)
Mn (*)	5.34 (5.42)	3.61 (4.73)	7.52 (8.50)	4.89 (3.00)
Cu (*)	12.99 (15.39)	9.13 (9.41)	9.59 (9.50)	4.40 (8.00)
Zn (*)	52.89 (100.48)	48.76 (103.89)	54.88 (113.20)	29.59 (116.70)
Sb (*)	5.34 (7.08)	3.11 (2.43)	3.48 (5.40)	2.85 (4.80)
V (*)	6.76 (8.35)	7.02 (8.81)	3.49 (3.10)	3.25 (2.90)
Co (*)	0.69 (1.39)	0.59 (1.42)	0.23 (0.22)	0.17 (0.20)
As (*)	2.18 (1.99)	1.93 (1.82)	0.95 (0.87)	0.73 (0.60)
Ba (*)	9.32 (10.03)	6.34 (7.02)	8.98 (8.00)	6.15 (5.20)
La (*)	0.30 (0.21)	0.17 (0.11)	0.30 (0.45)	0.20 (0.20)
Nd (*)	0.26 (0.20)	0.17 (0.09)	0.20 (0.35)	0.15 (0.10)
Dy (*)	0.31 (0.33)	0.25 (0.25)	0.08 (0.07)	0.07 (0.06)
Sr (*)	5.96 (6.94)	3.59 (3.96)	4.51 (14.10)	1.90 (2.20)
Th (*)	0.25 (0.14)	0.22 (0.11)	0.26 (0.28)	0.25 (0.25)
DTT _v	0.39 (0.23)	0.29 (0.19)	-	-
DTT _M	14.3 (6.0)	16.3 (7.4)	-	-
Ions	7.65 (3.57)	4.75 (2.51)	8.71 (4.54)	5.20 (3.12)
Metals	0.64 (0.57)	0.35 (0.34)	0.57 (0.65)	0.32 (0.26)
Total Carbon	6.53 (5.96)	5.70 (5.58)	6.51 (5.47)	5.62 (5.14)

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22 **Table S1.** Comparison of elements averages detected in the periods 2016-2017 and 2013-2014. In
23 parenthesis the standard deviations are reported. DTT_v is expressed in (nmol/min·m³); DTT_M is
24 expressed in (pmol/min· μg). (*) units are expressed in ng/m³.

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Location site	Reference	DTT _v (nmol/min·m ³)	
		PM ₁₀	PM _{2.5}
Lecce (Italy)	this study	0.39 (0.23)	0.29 (0.19)
Lecce (Italy)	Chirizzi et al., 2017	0.46 (0.32 – 0.80)	0.40 (0.29 – 0.72)
Lecce (Italy)	Pietrogrande et al., 2018	0.24 (0.12)	
Lecce (Italy)	Perrone et al., 2019	0.24 (0.04) cold season 0.22 (0.02) warm season	0.29 (0.03) cold season 0.19 (0.02) warm season
Lecce (Italy)	Romano et al., 2020	0.17 (0.05)	-
Sarno (Italy)	Cesari et al., 2019	-	0.19 (0.10)
Rome (Italy)	Jedynska et al., 2017	-	0.23 (0.11 – 0.34)
Milan (Italy)	Altuwayjiri et al., 2021	-	0.70 – 0.99
Milan (Italy)	Hakimzadeh et al., 2020	-	0.85 (0.19) warm season 3.38 (0.46) cold season
Po Valley (Italy)	Visentin et al., 2016	-	0.3 – 1.7
Trento (Italy)	Pietrogrande et al., 2021	0.33 (SD 0.07)	
Athens (Greece)	Paraskevopoulou et al., 2019	0.10 (0.09) PM _{2.5-10}	0.33 (0.20)
Athens (Greece)	Jedynska et al., 2017	-	0.28 (0.17 – 0.43)
Catalonia (Spain)	Jedynska et al., 2017	-	0.23 (0.07 – 0.69)
Paris (France)	Jedynska et al., 2017	-	0.23 (0.10 – 0.36)
Swiss	Daellenbach et al., 2020	3.16 (2.27)	1.82 (1.03)
Munich/Augsburg (Germany)	Jedynska et al., 2017	-	0.20 (0.00 – 0.45)
London/Oxford	Jedynska et al., 2017	-	0.14 (0.08 – 0.19)
Belgrade (Serbia)	Jovanovic et al., 2019	0.46 (0.29)	0.37 (0.15)
Netherlands	Jedynska et al., 2017	-	0.20 (0.13 – 0.29)
Copenhagen	Jedynska et al., 2017	-	0.21 (0.08 – 0.31)
Helsinki/Turku	Jedynska et al., 2017	-	0.15 (0.09 – 0.43)
Oslo	Jedynska et al., 2017	-	0.13 (0.06 – 0.25)
Ovest and Nord Europe	Weber et al., 2021	0.82 – 10.0 (*)	-

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27 **Table S2.** Comparison between DTT_v measured in PM_{2.5} and PM₁₀ collected in this study and in
28 other sites of Italy and Europe. In parenthesis it is reported the standard deviation or the min - max
29 interval. (*) The range is referring to different sites located in European countries.

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Source	β Coefficients (nmol/min·μg)	Std error (nmol/min·μg)	p-value
Biomass burning	0.012	0.002	<0.0001
Ammonium nitrate	0.014	0.003	<0.0001
Traffic	0.019	0.002	<0.0001
Sulphate	0.021	0.003	<0.0001
Marine	0.007	0.003	0.030
Crustal	0.008	0.003	0.006
Carbonates	0.019	0.006	0.001

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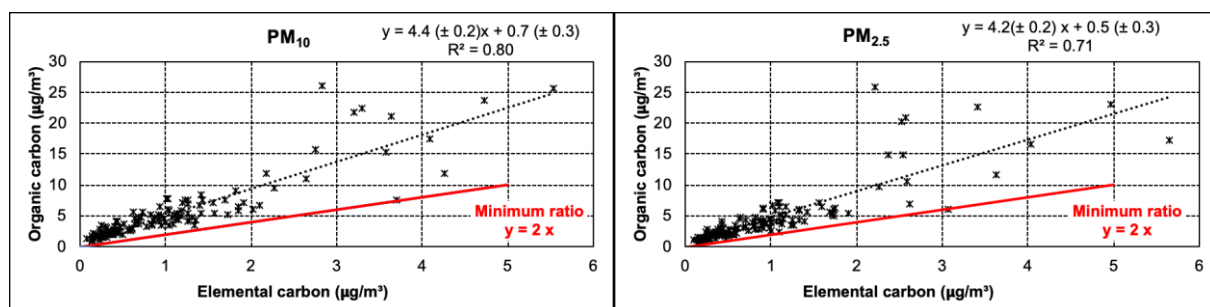
33 **Table S3.** Multi-linear regression (MLR) analysis results and parameters indicating the goodness of
34 the fit produced by the model for each source.

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Figure S1. Location of the Environmental-Climite Observatory (ECO), sampling site for this study.



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Figure S2. Correlation between OC and EC concentrations in PM₁₀ and in PM_{2.5}. Each graph includes the indication of the minimum OC/EC ratio (solid line) and a linear fit data (dashed line).

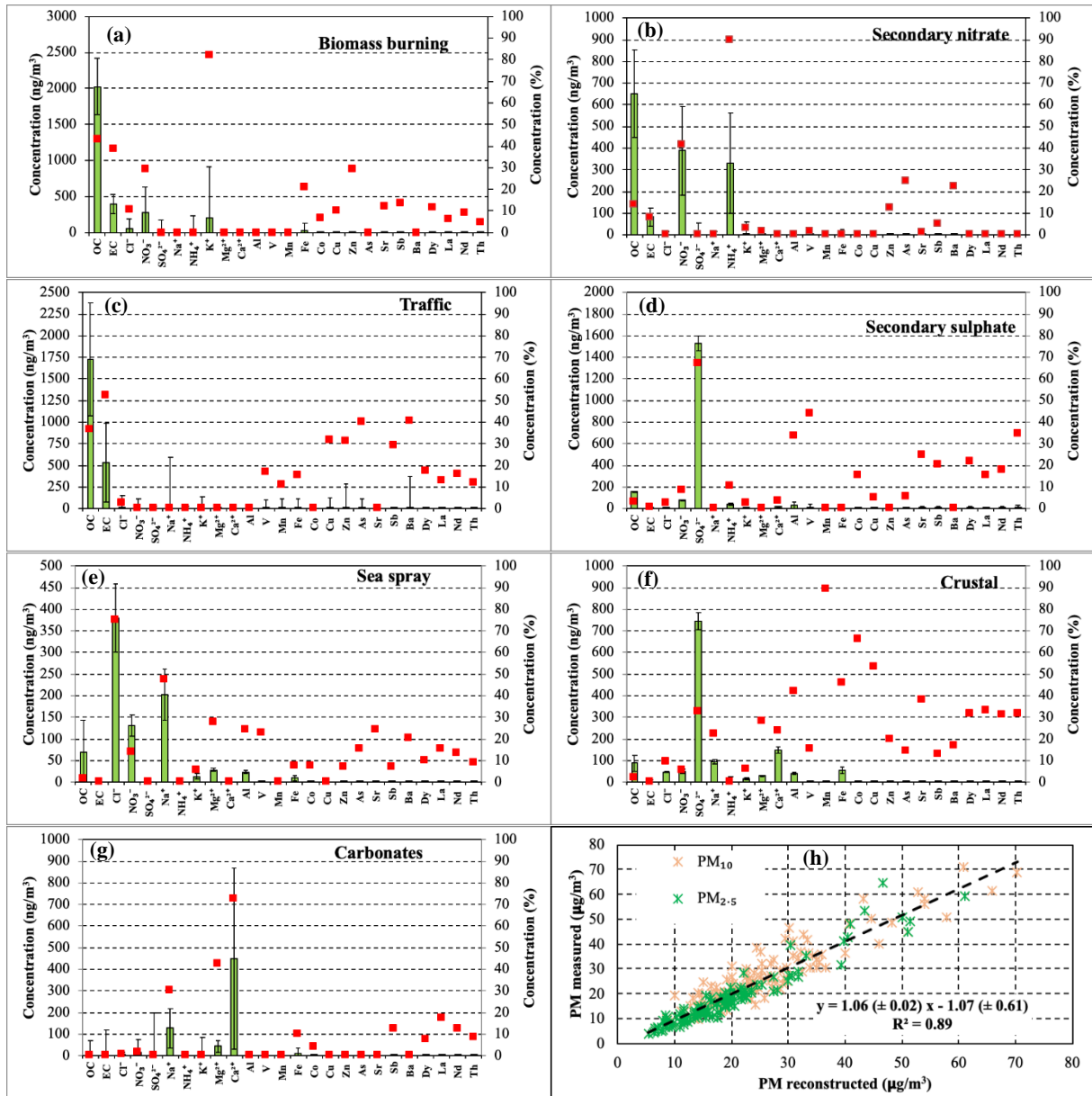


Figure S3. Factor/sources profiles obtained with PMF5 (a-g). Error bars represent uncertainty obtained with bootstrap method. The graph (h) reports a comparison between measured and reconstructed PM_{2.5} and PM₁₀ with a linear fit ($p < 0.001$).

Chemical analysis details

A punch (1 cm²) of one quarter of filter was used for determination of OC and EC using the thermo-optical transmittance (TOT) method (Sunset OC-EC Analyser), applying the EUSAAR2 protocol. The instruments were calibrated in the range 0-45 µgC/cm² using a sucrose standard solution. The LODs (Limit Of Detections) were 0.03 µg/m³ (EC) and 0.1 µg/m³ (OC) and typical measurement

74 uncertainties were 5% for OC and 10% for EC (Merico et al., 2019). OC and EC concentrations were
75 determined subtracting contamination on blank filters.

76 The second quarter of filter was used to extract the water-soluble fraction to be devoted both to
77 oxidative potential analysis and concentrations of water soluble ions determination. The water-
78 soluble fraction of collected PM was extracted in 15 mL of deionized water (Milli-Q 18 M Ω) using
79 a 30-min sonication. A portion of each extract was used in High Performance Ion Chromatography
80 (Dionex DX120 IC) system for determination of concentrations of major ions. The HPIC was
81 equipped with an ED50 Conductivity detector, used with a 25 μ L injection loop. Anions (Cl^- , NO_3^- ,
82 SO_4^{2-}) were separated with a Dionex AS4A-4 column coupled with an IonPac AG14 guard column
83 using as eluent 2.7 mM Na_2CO_3 and 1.0 mM NaHCO_3 in isocratic mode. Cations (Na^+ , NH_4^+ , K^+ ,
84 Mg^{2+} , Ca^{2+}) were separated with a Dionex CS12A-4 column with IonPac CG12A guard column,
85 using 20 mM MSA (methanesulfonic acid) as eluent in isocratic mode. The self-regenerating
86 suppressors Dionex ASRS 300 for anions and Dionex CSRS 300 for cations were used. HPIC
87 calibration was done using single anions and cations solutions (Thermo Scientific_Dionex_IC
88 Standard). The method detection limits (MDLs) values (g/L) were as follows: 8.5 (Na^+), 7.0 (K^+),
89 45.2 (NH_4^+), 9.2 (Ca^{2+}), 2.5 (Mg^{2+}), 4.9 (Cl^-), 10.5 (NO_3^-), and 52 (SO_4^{2-}).

90 Another portion of the water-soluble extracts was filtered with PTFE syringe filters (0.45 μm
91 porosity) to remove residual fibers and eventual insoluble materials. Successively, the filtered
92 aliquots were used to evaluate the oxidative potential (DTT assay) following the methodology of Cho
93 et al. (2005). Specifically, 3.5 mL of each extract was incubated at 37 ° C adding 0.5 mL of DTT
94 (1mM) and 1 mL of 0.5 M potassium phosphate buffer at pH 7.4 for times ranging from 5 to 90
95 minutes. At specific intervals (from 5 to 90 min), a 0.5 mL aliquot of the incubation mixture was
96 collected and 0.5 mL of trichloroacetic acid (10% w/v) was added to stop the reaction. Afterwards, 2
97 mL of 0.4M Tris-HCl, pH 8.9 containing 20 mM EDTA and 25 μ L of 10 mM DTNB was added and,
98 after 1 minute the absorbance of the solution was measured, at 412 nm, using a UV-Vis UVIKON

99 942 (KONTRON) spectrophotometer. The DTT depletion rate (δ_{DTT} , pmol/min) was determined by
100 linear regression between the measured absorbance and the time (Chirizzi et al., 2017). The detected
101 values of δ_{DTT} were corrected using field blank measurements. The uncertainty on δ_{DTT} , determined
102 by replication of measurements, was generally in the interval 3% - 15% (average ~ 6%). The DTT
103 depletion rate allows to calculate the OP in terms of DTT_V , i.e. activity normalized with the air volume
104 (V) actually sampled on each filter, or normalized with the mass of particulate matter collected on
105 the filter DTT_M .

106 The third quarter of filter was used in ICP-MS (NexIon 300X, Perkin Elmer, USA) to determine
107 concentration of different metals. Each sample was digested in closed Teflon vessels by a microwave
108 digester (Microwave Digestion System Start D, Milestone, Italy). The two steps procedure (EN
109 14385) was used. Firstly digestion in 1.2 mL HF (hydrofluoric acid, UltraTrace Analysis, 47%,
110 Honeywell Fluka™) plus 1.8 mL HNO_3 (UltraTrace Analysis, 65-71%, Honeywell Fluka™) using
111 temperature steps: from room temperature to 200 °C in 15 min, 15 min plateau at 200°C, and a final
112 cooling back to room temperature. Successively, after addition of 14 mL of saturated H_3BO_3 (Sigma
113 Aldrich, ACS reagent, $\geq 99.5\%$), temperature was increased to 200 °C in 10 min, a 15 min plateau
114 followed, and a final cooling to room temperature. Finally, samples were diluted to 25 mL in
115 volumetric flask using deionized water (Milli-Q® 18.2 M Ω). Each sample (1 mL) was transferred
116 into 10 mL volumetric flask, Rh (Fluka, Spectroscopic Grade) (final concentration 5 $\mu\text{g/L}$) as internal
117 standard and Y (Fluka, Spectroscopic Grade) (final concentration 5 $\mu\text{g/L}$ - Indium in case of rare
118 earth elements analysis-) as second control were added and make up to the mark with 2% HNO_3
119 solution. The ICP-MS was tuned using a Multi-Element Standard for Instrument Calibration solution
120 (Perkin Elmer) at 1 $\mu\text{g/L}$: Be, Ce, Fe, In, Li, Mg, Pb, U. The external calibration was performed for
121 the following elements: Al, As, Ba, Cd, Ce, Co, Cu, Dy, Fe, La, Li, Mn, Nd, Pb, Sb, Sr, Th, Ti, V,
122 Zn using rare earth elements mix (Perkin Elmer) and single analyte standard solutions (Fluka,
123 Spectroscopic Grade). Quality control checks were performed monitoring the intensities of all

124 internal standards for every sample analysis and analyzing the laboratory control samples (LCS), in
125 each sample batch, at a frequency of one LCS every 10 samples. The LCS were pre-fired quartz filters
126 digested using the same procedure used for samples and a mix of standards, selected to control both
127 matrix effect and possible memory effect. The MDLs, calculated with the same approach used for
128 anions and cations, were between 0.007 µg/L (La) and 1.3 µg/L (Al).

129 Final concentrations of the different chemical species were corrected using the average level
130 found in the blank samples. The concentration of a specific species in a samples was substituted with
131 the threshold value $\sigma_B/2$ (i.e. one half of the standard deviation in blank filters) when it was too low
132 to be quantified. Uncertainties for measured concentrations were evaluated as described in Cesari et
133 al. (2018b).

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135 **PMF analysis details**

136 The species OC, EC, Cl, SO_4^{2-} , NH_4^+ , K^+ , Mg^{2+} , Ca^{2+} , Mn, Fe, As, and Ba, were classified as
137 “strong” and used directly in PMF5; while, the species NO_3^- , Na^+ , Al, V, Co, Cu, Zn, Sr, Sb, Dy, La,
138 Nd, and Th were “weak”. The best solution for the base run was obtained using seven factors: biomass
139 burning, ammonium nitrate, traffic, sulphate, sea spray, crustal, and carbonates. Compared to the
140 previous dataset, only the industrial source is missing likely because Pb (one of its main markers)
141 was not available in the “2016-2017” dataset. Successively, a constrained run was performed in order
142 to improve the separation between factors profiles (Amato et al., 2016; Cesari et al., 2021). The
143 constraints used were: pull down maximally OC in traffic factor; pull up maximally SO_4^{2-} and Mg in
144 crustal factor profile; pull down maximally OC in carbonate factor; pull up maximally NH_4^+ in
145 secondary sulphate factor. The final dQ change, compared to the base run, was 7.8%. Uncertainty
146 estimates in PMF results were obtained with the bootstrap method (Paatero et al., 2014). The
147 bootstrap of the “constrained solution” (applied with 100 runs with random seed, block size suggested

148 23, and $R=0.6$) gave a good mapping of the solution with unmapped cases limited to 1% and 2% for
149 traffic and nitrate (respectively) and to 6% (crustal) and 4% (carbonates).

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