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Abstract: This work investigates n-alkanes in the range C₁₄-C₃₂, polycyclic aromatic hydrocarbons (PAHs) and nitrated PAHs (nitro-PAHs) composition of PM_{2.5} and PM₁ collected in the surroundings of a municipal waste incinerator close to Bologna (Northern Italy). The particulate matter was sampled in eight stations: one of these was located inside the urban area of Bologna, while the others were placed in a domain of 8x9 km² around the incinerator plant. Two monitoring campaigns were carried out, in summer 2008 and in winter 2009. In each campaign, two stations were placed in zones of maximum impact of plant emissions and other two ones as their controls. The study of n-alkanes in atmospheric particulate was performed to understand the contribution of anthropogenic and biogenic sources, PAHs and nitro-PAHs were selected to investigate PM composition near an incinerator plant. Higher concentrations of PAHs and, to a less extent, of n-alkanes were measured in the cold season. This can be due to several reasons, namely, an increased combustion of fossil fuel during wintertime, stagnant atmospheric conditions and lower temperatures that not only favour gas-to-particles partitioning but also reduce atmospheric reactivity. The impact of combustion in the cold season was also confirmed by the higher percentage content of PAHs in PM₁ than in PM_{2.5}. On the contrary, higher amount of nitro-derivatives were measured in summer than in winter, suggesting that the contribution of secondary aerosol is not negligible in the hot season. The most abundant n-alkanes were the long-chain homologues (>C₂₇) deriving from anthropogenic sources as indicated by the Carbon Preference Indexes. In both seasons, the sites chosen as controls were characterized by higher concentrations of PAHs than the respective maxima suggesting that extra-incinerator sources, especially vehicles emissions, are the main responsible for PAHs in PM_{2.5}. On the contrary, in winter, PM₁ was enriched in PAHs in the site close to the incinerator with respect to its control.

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DI FERRARA
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Dear Chak K Chan
Editor-in-Chief
Atmospheric Environment

We would like to thank you for having considered our manuscript for publication on Atmospheric Environment journal.

We deeply considered all the points paid to our attention by the Reviewer. The manuscript was modified to account for all the Reviewer suggestions and the details are reported in the Response to Reviewers file.

Best Regards

Prof. Luisa Pasti

A handwritten signature in blue ink that reads "Luisa Pasti". The signature is written in a cursive style and is positioned above a horizontal line.

Responses to Reviewers

Re-review comments:

Organics, such as PAHs and the nitrated and oxygenated derivatives, are considered important harmful component of PM. This manuscript reported these pollutants in PM_{2.5} and PM₁ sampled in the surroundings of a municipal waste incinerator in the Northern Italy, and it provided some valuable information regarding this important pollution form. In addition, in the revised manuscript, some major concerns especially those on QAQC were well addressed. Therefore I recommend publishing it in Atmospheric Environment.

We thank the Reviewer for His/Her positive comment.

The following are some specific comments:

Line 181: Suggest to provide a more detailed information on UNI EN 15549:2008 in the reference section. Also in lines 185 and 250.

Thank you, it was a mistake. The details of UNI EN 15549:2008 and EPA 3630C methods were added in the references section, in particular:

- *p. 26 lines 857-862: “UNI EN 15549:2008. Air Quality - Standard method for the measurement of the concentration of benzo[a]pyrene in ambient air. <http://store.uni.com/magento-1.4.0.1/index.php/uni-en-15549-2008.html>” and “US- EPA (US- Environmental Protection Agency), 1996. Test Method 3630C: Silica Gel Cleanup. <https://www.epa.gov/sites/production/files/2015-12/documents/3630c.pdf>”*

Line 182 and 183: Only one extraction? I'm afraid the extraction efficiency could be low. Did the author check the efficiency, for instance through twice extractions?

Thank you for having pointed to this. The extraction was performed in two successive steps. The text has been amended at p. 6 line 180.

Lines 262 to 264: Planetary Boundary Layer depth is very important on pollution concentrations. Suggest to provide some further information on the measurement of this parameter, or provide related reference.

At p. 8 lines 260-261, the sentence “Mixing layer height was estimated using the preprocessor CALMET by ARPAE Emilia-Romagna (Scire et al., 2000; Deserti et al., 2001).” was added. The above-cited works have been added in the references section, in detail:

- *p. 22 lines 707-710: “Deserti M., Savoia E., Cacciamani C., Golinelli M., Kerschbaumer A., Leoncini G., Selvini A., Paccagnella T., Tibaldi S., 2001. Operational meteorological preprocessing at Emilia-Romagna ARPA meteorological service as a part of a decision support system for air quality management. International Journal of Environment and Pollution 16, 571-582.”*
- *p. 25 lines 813-814: “Scire, J. S., Robe, F. R., Fernau, M. E., Yamartino, R. J., 2000. A User Guide for the CALMET Meteorological Model (Version 5). Earth Tech, Inc.”*

Line 311: Please define CPI here.

CPI was defined at p. 10 line 306.

Lines 433, 434, and 460 to 462: Suggest replace % with ppm because it's hard for author to follow these data with so many decimals.

The percentages have been replaced with $\mu\text{g g}^{-1}$ at p. 13 lines 429-431 and at p. 14 lines 456-458.

1 **Determination of n-alkanes, PAHs and nitro-PAHs in PM_{2.5} and PM₁ sampled in**
2 **the surroundings of a municipal waste incinerator**

3
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35 **Abstract**

36 This work investigates n-alkanes in the range C14-C32, polycyclic aromatic hydrocarbons (PAHs)
37 and nitrated PAHs (nitro-PAHs) composition of PM_{2.5} and PM₁ collected in the surroundings of a
38 municipal waste incinerator close to Bologna (Northern Italy). The particulate matter was sampled
39 in eight stations: one of these was located inside the urban area of Bologna, while the others were
40 placed in a domain of 8x9 km² around the incinerator plant. Two monitoring campaigns were
41 carried out, in summer 2008 and in winter 2009. In each campaign, two stations were placed in
42 zones of maximum impact of plant emissions and other two ones as their controls. The study of n-
43 alkanes in atmospheric particulate was performed to understand the contribution of anthropogenic
44 and biogenic sources, PAHs and nitro-PAHs were selected to investigate PM composition near an
45 incinerator plant. Higher concentrations of PAHs and, to a less extent, of n-alkanes were measured
46 in the cold season. This can be due to several reasons, namely, an increased combustion of fossil
47 fuel during wintertime, stagnant atmospheric conditions and lower temperatures that not only
48 favour gas-to-particles partitioning but also reduce atmospheric reactivity. The impact of
49 combustion in the cold season was also confirmed by the higher percentage content of PAHs in PM₁
50 than in PM_{2.5}. On the contrary, higher amount of nitro-derivatives were measured in summer than in
51 winter, suggesting that the contribution of secondary aerosol is not negligible in the hot season. The
52 most abundant n-alkanes were the long-chain homologues (>C27) deriving from anthropogenic
53 sources as indicated by the Carbon Preference Indexes. In both seasons, the sites chosen as controls
54 were characterized by higher concentrations of PAHs than the respective maxima suggesting that
55 extra-incinerator sources, especially vehicles emissions, are the main responsible for PAHs in
56 PM_{2.5}. On the contrary, in winter, PM₁ was enriched in PAHs in the site close to the incinerator with
57 respect to its control.

58
59 **Keywords**

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61
62 **1. Introduction**

63 The incineration process can result in three potential sources of exposure: emissions to the
64 atmosphere, solid ash residues and cooling water. Provided that solid ash residues and cooling water
65 are appropriately handled and disposed of, atmospheric emissions remain the only significant route
66 of exposure to people. The combustion gives rise to fine particles that can have negative effect on
67 human health due to their size and composition (Laden et al., 2000; Morawska and Zhang, 2002). In
68 particular, during incomplete combustion of fossil fuels and biomass, polycyclic aromatic

69 hydrocarbons (PAHs) can be released into the atmosphere (Jedynska et al., 2014), partitioned
70 between the vapour phase and the particle matter (the partition coefficient strongly depends on the
71 PAH molecular weight) (Masiol et al., 2012; Cvetković et al., 2015). These compounds are of great
72 concerns: the United States-Environmental Protection Agency (US-EPA) classified 16 PAHs as
73 priority pollutants based on toxicity, potential for human exposure, frequency of occurrence at
74 hazardous waste sites and the extent of available information (EPA, 2014). Among these 16 PAHs,
75 US-EPA considers 7 (i.e. benzo[a]anthracene, chrysene, benzo[a]pyrene, benzo[b]fluoranthene,
76 benzo[k]fluoranthene, dibenz[a,h]anthracene, and indeno[1,2,3-cd]pyrene) as probable human
77 carcinogens (EPA, 2014).

78 Analogously, nitro-PAHs originate primarily as direct or indirect products of incomplete
79 combustion, through nitration during combustion processes (e.g. in vehicle exhaust, aircraft
80 emissions, industrial emissions, domestic residential heating/cooking, wood burning) (WHO, 2003).
81 Nitro-PAHs can also originate through atmospheric formation either by gas-phase reactions or by
82 heterogeneous gas-particle interaction of parent PAHs with nitrating agents (WHO 2003; Reisen
83 and Arey, 2005).

84 Nitro-PAHs as well as their corresponding parent-PAHs are known to have toxic, carcinogenic and
85 estrogenic properties (Bandowe et al., 2014). Furthermore, nitro-PAHs are direct acting mutagens
86 and also produce reactive oxygen species which in turn are also toxic (WHO, 2003).

87 Because of the possible presence of these contaminants in the incinerator emissions and of their
88 toxicity, there is a high perception of health risk, especially for people living nearby these plants.
89 Although this is a very felt issue, many studies state that “modern, well managed incinerators make
90 only a small contribution to local concentrations of air pollutants. It is possible that such small
91 additions could have an impact on health but such effects, if they exist, are likely to be very small
92 and not detectable” (HPA, 2009). However, it should also be considered that location,
93 meteorological conditions and plant characteristics can play an important role on the emissions
94 characteristics. Moreover, in the literature the works concerning the PAHs and nitro-PAHs
95 composition of PM collected in area close to an incinerator are relatively scarce, especially in Italy,
96 and only few of them deal with PM₁, which is generally known as harmful for human health (Chen
97 et al., 2016). In order to acquire new knowledge about the air quality in the proximity of
98 incinerators, the local Emilia Romagna (ER) Administration promoted a wide research project
99 called MONITER (<http://www.arpae.it/monitor/>). In particular this work, which is a part of the
100 MONITER project, reports the content of PAHs and nitro-PAHs in PM₁ and PM_{2.5} collected in the
101 neighbourhood of a Municipal Waste to Energy Incinerator (WTE) located in the ER region.
102 Additionally, to differentiate the potential sources of these contaminants, the composition in n-

103 alkanes of the particulate was also evaluated. It is well known that n-alkanes can be emitted from
104 anthropic or natural (mostly vegetal) sources and, for this reason, they are considered useful in
105 tracking the origin of atmospheric aerosol (Simoneit, 1989; Duan et al., 2010). In particular, the
106 abundance distribution of the odd/even terms is a key diagnostic parameter in discriminating
107 between the biogenic and anthropogenic nature of n-alkanes sources (Pietrogrande et al., 2010).
108 The aim of this work is to evaluate the effect of a WTE on PM composition by comparing the
109 concentrations of organic compounds (i.e. n-alkanes, PAHs and nitro-PAHs) in the aerosol
110 collected at different sites in a domain of about 10 km² around WTE location, in two different
111 seasons.

112

113 **2. Materials and Methods**

114 **2.1 Sampling of particulate matter**

115 The incineration plant under study is located in a suburban–farming area, less than 10 km away
116 from northeast of Bologna (Italy), in the Po Valley, which is a well–known polluted critical area.
117 The plant has the following main features: 600 tons day⁻¹ of incinerating capacity, two 80m–high
118 stacks and BAT (Best Available Technique) purification devices. In particular, the gas treatment
119 system consists of a bag filter dedusting and an oxygen content controlled post-combustion
120 chamber continuously set at a temperature over 850 °C in turbulence condition ([http://ippc-
121 aia.arpa.emr.it/DettaglioAutorizzazionePub.aspx?id=46422](http://ippc-aia.arpa.emr.it/DettaglioAutorizzazionePub.aspx?id=46422)).

122 A preliminary study with ADMS–Urban (Cerc, Cambridge, UK) dispersion model was performed
123 to select the coordinates of incinerator maximum impact and the related control sites, evaluating
124 PM₁₀ and NO_x emissions as pollutant tracers.

125 ADMS simulations were used with the aim to maximize prospective gravimetric differences of
126 coupled max and control sites, not to modelling air quality over the domain. Background
127 concentrations (i.e. due to emissions not included in the domain) have been assumed uniform in the
128 domain and not modelled. Further details of the procedure are described elsewhere (Rossi et al.,
129 2012; Bonafè and Rossi, 2011). The remaining sites were chosen using the diffusion maps as a
130 qualitative guide, under the same hypothesis and limitations above described.

131 Seven out of eight monitoring stations were placed in a domain of 8x9 km² around the plant; the
132 eighth station (MGA) was located inside the urban area of Bologna, in a site used for urban
133 background measurements by ARPAE-ER (Emilia Romagna - Regional Agency for Prevention,
134 Environment and Energy).

135 The seven monitoring stations inside the domain were chosen based on the following criteria:

- 136 • MXW is representative of the maximum impact of plant emissions, in terms of
137 concentration at the ground level, in the meteorological winter conditions.
- 138 • CTW is selected as follows:
- 139 i) the estimated impact of the relevant confounding emissions included in the domain
140 should be similar to MXW (with a tolerance of +/-25%);
- 141 ii) the estimated impact of the incinerator should be minimum.
- 142 Therefore, CTW is used as a "control" of MXW.
- 143 • MXS was chosen as MXW but in the meteorological summer conditions.
- 144 • CTS was chosen as a "control" of MXS, with the same criteria as CTW.
- 145 • MXD represents the most polluted site of the domain.
- 146 • MND is surrounded by agricultural land, so it represents a rural area of the domain.
- 147 • CAS is located in a suburban area.

148 The locations of the monitored sites are shown in Figure 1.

149 A more detailed description of the monitoring stations is reported in previous works (Rossi et al.,
150 2012; Sarti et al., 2015).

151

152 **FIG 1**

153

154 The sampling campaign was conducted in summer from the 3rd of June to the 24th of July 2008 and
155 in winter from the 14th of January to the 12th of March 2009. In both seasons, gravimetric
156 evaluations on samples were performed on 24h basis (Rossi et al., 2012).

157 PM₁ samples were collected solely in MXW, MXD and CTW sites and are notated as MXW-1,
158 MXD-1 and CTW-1, respectively. The PM_{2.5} samples collected in the above-mentioned three sites
159 are notated as MXW-2.5, MXD-2.5 and CTW-2.5. For all the other sites (e.g., CAS, CTS, MGA,
160 MND, and MXS), only PM_{2.5} was sampled.

161 The PM was collected daily on quartz fiber filters 47 mm diameter (*Whatman*, Maidstone, UK)
162 through Skypost PM TRC Tecora low volume outdoor samplers (*Tecora*, Paris, France), at airflow
163 rate of 38 L min⁻¹ for 24 h (corresponding to $\approx 55 \text{ m}^3 \text{ day}^{-1}$). Sampler head was placed 2 m above to
164 the ground level.

165 For each sampler, except MXW-2.5, chemical analyses were performed by using filters from two
166 consecutive days (analysis on 48h time basis). A quarter of filter of one day was pooled together
167 with a quarter of a filter of the subsequent day (Sarti et al., 2015) before analysis. For MXW-2.5
168 chemical analyses were performed on 24h time basis. In this case, two coupled samplers have been
169 used and the two filters of the same day underwent to the same procedure above described. The

170 frequency of analysis of MXW-2.5 was increased since simulations indicated this site as
171 representative of maximum deposition of plant emissions, under averaged meteorological
172 conditions (Rossi et al., 2012). The choice of combining two filters together derives from the
173 necessity of performing chemical analyses on a wide number of analytes by several laboratories.
174 In this work, the mean values of every pollutant over the same periods of time were compared for
175 all the sampling sites.

177 **2.2 Analytical procedure**

178 The n-alkanes ranging from C14 and C32, twenty-three PAHs and four nitro-PAHs have been
179 quantified. Chemical analyses were carried out according to UNI EN 15549:2008. Portions of filters
180 of two subsequent days (see above) were extracted twice in 50 ml of dichloromethane (*Merck*,
181 Darmstadt, Germany) in an ultrasonic bath for 10 minutes at room temperature. The extract was
182 concentrated by a rotary evaporator and purified by chromatography on a packed column in silica
183 gel (length 10 cm, diameter 1 cm), deactivated at 3% with water, according to EPA 3630C method
184 (US-EPA, 1996). The purification process leads to two fractions, the first one eluted with 15 ml of
185 n-hexane (*Sigma Aldrich*, Steinheim, Germany) contains n-alkanes, and the second one, containing
186 PAHs and nitro-PAHs, was eluted with 30 ml of a mixture toluene:dichloromethane 80:20 (*Merck*,
187 Darmstadt, Germany). Each fraction was dried under a gentle stream of nitrogen and then dissolved
188 in 200 μ l of toluene with known amounts of internal standards. The selected internal standards were
189 perdeuterated n-tetracosane (*Sigma Aldrich*, Steinheim, Germany) for n-alkanes, naphthalene-d₈,
190 fluorene-d₁₀, fluoranthene-d₁₀ and perylene-d₁₂ (*o2si*, Charleston, SC, USA) for PAHs, 3-
191 nitrofluoranthene-d₉ and 2-nitrofluorene-d₉ (*Cambridge Isotope Laboratories Inc.*, Andover, MA,
192 USA) for nitro-PAHs analysis.

193 During the whole treatment, samples were protected from light to avoid photochemical degradation
194 and they were stored in refrigerator at 4°C until the analysis.

195 The determination of n-alkanes and PAHs was carried out by gas chromatography-mass
196 spectrometry (GC-MS) on a GC Agilent 6890N (*Agilent Technologies*, Santa Clara, CA, USA)
197 coupled with a MS 5973N Agilent quadrupole mass spectrometer. The separation was performed on
198 a Agilent DB-5-MS fused silica capillary column (length 60 m, i.d. 250 μ m, film thickness 0.25
199 μ m). The injector was kept at 250 °C and 1 μ L of sample was injected in pulsed splitless mode.
200 Helium (purity 99.99 %) was used as carrier gas with a constant flow of 1.2 ml min⁻¹.

201 The n-alkanes analysis was performed under the following temperature program: (1) temperature
202 ramp from 60 °C to 300 °C at 10 °C min⁻¹, (2) 300 °C hold for 75 minutes. The MS source operated
203 with electron ionization (EI) and the temperature was kept at 230 °C. The temperature of the

204 quadrupole MS was kept at 150 °C. The chromatograms were acquired in the selective ion
205 monitoring (SIM) mode.

206 The PAHs analysis was performed under the following temperature program: (1) 70 °C hold for 4
207 minutes, (2) temperature ramp from 70 °C to 300 °C at 10 °C min⁻¹, (3) 300 °C hold for 31 minutes.

208 The MS source operated with electron ionization (EI) and the temperature was kept at 230 °C. The
209 temperature of the quadrupole MS was kept at 150 °C. The chromatograms were acquired in the
210 selective ion monitoring (SIM) mode. The SIM program was designed to monitor the molecular
211 [M]⁺ and isotopic [M+1]⁺ ions. It hasn't been possible to resolve the isomer benzo[b]fluoranthene
212 from benzo[j]fluoranthene (in the following notated as benzo[b+j]fluoranthene) and the isomer
213 dibenzo[a,c]anthracene from dibenzo[a,h]anthracene (notated as dibenzo[a,c+a,h]anthracene).

214 Nitro-PAHs determination was carried out by gas chromatography-mass spectrometry (GC-MS) on
215 a GC Agilent 6890N coupled with a MS PolarisQ ionic trap Thermo Fisher (*Thermo Fisher*
216 *Scientific Inc.*, Waltham, MA, USA) (Feilberg et al., 2001; Bamford and Baker, 2003). The
217 separation was performed on a Agilent DB-5-MS fused silica capillary column (length 60 m, i.d.
218 250 µm, film thickness 0.25 µm). The injector was kept at 250 °C and 5 µL of sample were injected
219 in pulsed splitless mode. Helium was used as carrier gas with a constant flow of 1.2 ml min⁻¹. The
220 nitro-PAHs analysis was performed under the following temperature program: (1) 70 °C hold for 1
221 minute, (2) temperature ramp from 70 °C to 300 °C at 10 °C min⁻¹, (3) 300 °C hold for 25 minutes.
222 The ionic trap operated in negative chemical mode, with methane as reagent gas. The
223 chromatograms were acquired in the selective ion monitoring (SIM) mode. The SIM program was
224 designed to monitor the molecular [M]⁺ and isotopic [M+1]⁺ ions. Fragmentation voltages were
225 selected by analysing standards at increasing fragmentation voltages. The voltages that gave the
226 highest abundance of fragment ions were chosen for quantitation.

227 All analytes were identified by comparison of both retention times and mass spectra of reference
228 standards: n-alkanes standard solutions were purchased from *Supelco* (Milan, Italy), while PAHs
229 and nitro-PAHs standard solution were purchased from *ULTRA Scientific* (North Kingstown, RI,
230 USA). The quantification was based on five independent calibration solutions containing analytes at
231 different concentrations. Internal standards deuterium-labeled compounds (see above) were added
232 to each sample, blank and calibration solutions.

233

234 **2.3 Quality assurance**

235 The detection limits (LODs) of analytes, calculated as 3 times the average noise level (Feilberg et
236 al., 2001), were 0.08 ng m⁻³ for n-alkanes, 0.002 ng m⁻³ for PAHs and 0.004 ng m⁻³ for nitro-PAHs.

237 In order to quantify procedural recoveries, known volumes of surrogate standard solutions were
238 added to samples prior to extraction. The recoveries of the spiked solutions were 79 ± 20 % for n-
239 alkanes, 92 ± 27 % for PAHs and 105 ± 30 % for nitro-PAHs, by using 5 α -androstane,
240 benzo[a]pyrene-d12 and 4-nitro-para-terphenyl (*Sigma Aldrich*, Steinheim, Germany), respectively,
241 as surrogates. Since satisfying recoveries were obtained, analyte concentrations in samples were not
242 surrogate-corrected.

243 A possible contamination due to collection, transport, and extraction of samples was evaluated by
244 analyzing reagent blanks, lot blanks (i. e. clean unexposed filters) and field blanks (i. e. filters not
245 used in PM sampling but submitted to the same manipulation as the samples). Blank concentrations
246 of benzo[a]pyrene were below 3% of the target value (UNI EN 15549:2008). The reagent blank has
247 been subtracted from the value of concentration in samples.

248 In data handling, concentrations of analytes below the detection limits were assumed equal to 1/2 of
249 LOD (Lampa et al., 2012).

250

251 **2.4 Meteorological conditions**

252 The Po Valley is characterized by frequent stagnant atmospheric conditions especially during
253 wintertime, when episodes of thermal inversions at low altitude, low mixing layer heights (H_{mix})
254 and low wind velocity occur (Vecchi et al., 2004). This atmospheric stability leads to an
255 accumulation of pollutants to the first hundred meters of the atmosphere and to condensation of
256 semi-volatile species, causing high PM episodes (Perrone et al., 2012; Pietrogrande et al., 2015).

257 In Table S1, average meteorological data measured by ARPAE-ER at the urban station in Bologna
258 are shown. The winter campaign was characterized by lower Planetary Boundary Layer depth (H_{mix}
259 ranging from 300 m in January to 627 m in March), while in summer higher values of H_{mix} were
260 measured (mean value 924 m). Mixing layer height was estimated using the preprocessor CALMET
261 by ARPAE-ER (Scire et al., 2000; Deserti et al., 2001).

262 Temperatures showed significant variations from the colder winter (mean value 6.98 °C) to the
263 warmer summer (mean value 24°C). Also the daily solar radiation, responsible for photochemical
264 reactions of organic pollutants, showed strong seasonality with low values in the cold season
265 (ranging from 389 W m⁻² in January to 742 W m⁻² in March), in comparison with higher values in
266 summer (937 W m⁻²).

267

268 **3. Results**

269 In previous works (Rossi et al., 2012; Sarti et al., 2015), the concentrations of particulate matter
270 (PM_1 and $PM_{2.5}$) and their seasonal and spatial variations in the sampling sites of the domain have

271 been reported. Some relevant results are herein briefly recalled: the $PM_{2.5}$ amount is higher in
272 winter than in summer (averaged values of $33.7 \pm 1.9 \mu\text{g m}^{-3}$ and $19.68 \pm 0.78 \mu\text{g m}^{-3}$ respectively)
273 and the PM_1 fraction accounts for the 79% in summer and for the 66% in winter of $PM_{2.5}$. In the
274 following the n-alkanes, PAHs and nitro-PAHs composition of $PM_{2.5}$ and PM_1 is discussed. The
275 average concentrations and the standard deviations of the analytes herein investigated are reported
276 in Supplementary Information (Tables S2, S3 and S4).

277 The statistical elaborations presented in this work were carried out through MATLAB® ver. 7
278 software (The Mathworks, Inc., Natick, MA, USA).

279

280 **3.1 n-alkanes**

281 The sum of all n-alkanes (i.e. C14-C32) detected in summer is 61 ng m^{-3} in $PM_{2.5}$ and 49 ng m^{-3} in
282 PM_1 and they constitute the 0.31% and 0.32% of $PM_{2.5}$ and PM_1 respectively. In winter, these
283 amounts are 165 ng m^{-3} (0.49%) in $PM_{2.5}$ and 72 ng m^{-3} (0.32%) in PM_1 . All the values have been
284 calculated on the basis of the values averaged on all the sampling sites ($PM_{2.5}$: MXW-2.5, CAS,
285 CTS, CTW-2.5, MGA, MND, MXD-2.5 and MXS; PM_1 : MXW-1, CTW-1 and MXD-1). These
286 quantitative results indicate a larger concentration of alkanes in $PM_{2.5}$ in the cold season. Higher
287 concentrations of alkanes in $PM_{2.5}$ collected in winter with respect to that sampled in summer were
288 also observed in Thessaloniki (Chrysikou and Samara, 2009), in Milan (Perrone et al., 2012) and in
289 Rome (Cecinato et al., 1999). This finding can be related to the increase in source emission from
290 combustion and to stable meteorological conditions in the cold season which are unfavourable for
291 the pollutants dispersion, as discussed in Paragraph 2.4.

292

293 **FIG 2**

294

295 The averaged concentrations of each n-alkane in $PM_{2.5}$ sampled in the sites of the domain during the
296 summer and winter are reported in Figures 2a and 2b, respectively. Figure 2c and 2d show the mean
297 concentrations of n-alkanes in the sampling sites during the two campaigns. It can be noted that, in
298 MXD in summer (Fig. 2c) and in MXW in winter (Fig. 2d), the total concentration of n-alkanes in
299 PM_1 is slightly higher than that in $PM_{2.5}$. This finding indicates that the n-alkanes in the two
300 samples are preferentially partitioned in PM_1 , the small differences between PM_1 and $PM_{2.5}$ can
301 arise from the measurement errors.

302 By comparing Figs. 2a and 2c, it can be seen that in summer there is a predominance of even terms
303 among short-chains n-alkanes (<C25). In winter, the concentrations of long-chain alkanes are
304 generally higher than short-chain ones (see Figs. 2b and 2d).

305 To investigate on the possible sources classification (i.e. anthropogenic or biogenic) of n-alkanes,
 306 the Carbon Preference Index (CPI), describing the abundance distributions of the odd/even terms,
 307 was calculated for all the sites in both seasons. In addition to the CPI calculated for all the analysed
 308 homologues (CPI₁₅₋₃₂), the Carbon Preference Index for biogenic/pyrogenic (CPI₂₅₋₃₂) and for
 309 petrogenic n-alkanes (named CPI₁₄₋₂₅) have been calculated as follows (Górka et al., 2014):

$$310 \quad CPI_{15-32} = \frac{\sum(C_{15} - C_{31})}{\sum(C_{16} - C_{32})} \quad (1)$$

$$311 \quad CPI_{25-32} = \frac{\sum(C_{25} - C_{31})}{\sum(C_{24} - C_{32})} \quad (2)$$

$$312 \quad CPI_{14-25} = \frac{\sum(C_{15} - C_{25})}{\sum(C_{14} - C_{24})} \quad (3)$$

313 Anthropogenic emissions from fossil fuel combustion generate a random distribution of odd vs.
 314 even terms yielding CPI₁₅₋₃₂ values close to 1. On the other hand, hydrocarbons originated from
 315 terrestrial plant material show a predominance of odd-numbered terms showing CPI₁₅₋₃₂ values
 316 higher than 3 (Simoneit, 1989).

317 Another useful parameter to discriminate between biogenic and anthropogenic sources is the plant
 318 wax n-alkanes content (named %WNA). It has been calculated from the following equation
 319 according to Simoneit et al. (1991).

$$320 \quad \%WNA = \frac{\sum_n \left(C_n - \frac{C_{n+1} + C_{n-1}}{2} \right)}{\sum_m C_m} \cdot 100 \quad (4)$$

321 where n = 25, 27, 29, 31 and m = 14, ..., 32.

322

323 The odd carbon number n-alkanes with more than 25 carbon atoms are the most prominent wax n-
 324 alkanes identified in emissions from the vegetation of the leaf composites (Cincinelli et al., 2007;
 325 Rogge et al., 1993b). High %WNA values indicate a greater contribution of biogenic sources.

326 The most abundant alkane (named C_{max}), the CPI values and %WNA are reported in Table 1 for all
 327 the stations in summer and winter.

328

329 **TABLE 1**

330

331 Regarding CPIs it can be observed that in summer (see Table 1a) they follow a trend CPI₂₅₋₃₂ >
 332 CPI₁₅₋₃₂ > CPI₁₄₋₂₅ for all the sites, whereas in winter (Table 1b) the differences in CPIs are less
 333 significant. For most of the sites of the domain, CPI₂₅₋₃₂ values slightly decrease in winter with

334 respect to summer. This finding indicates that, for long-chain alkanes, the contribution of biogenic
335 sources is more relevant in the warm season than in the cold one. On the contrary, CPI_{15-32} and
336 CPI_{14-25} generally increase in the cold season, with values below 3, indicating that n-alkanes <C25
337 were primarily originated from fuel combustion processes.

338

339 **3.1.1 n-alkanes in summer**

340 The low value of CPI_{25-32} in MXW-2.5, together with the highest total concentration of the
341 homologues >C25 measured in this site (see Figure 2c) in summer, indicates that long-chain alkanes
342 detected in MXW-2.5 have mainly pyrogenic source (biomass combustion) rather than biogenic one
343 (mechanical abrasion of leaf wax) (Górka et al., 2014). From Table 1a it can also be noted that in
344 summer, CTW-2.5 is the only site having a $CPI_{25-32} > 3$. From this value it can be inferred that long-
345 chain alkanes are mainly of biogenic origin (Górka et al., 2014). This aspect is furthermore
346 confirmed by the highest %WNA equal to 48%, together with the C_{max} of C29, which is one of the
347 n-alkanes typically emitted by wax-leaf abrasion (Rogge et al., 1993b).

348 MGA and MXD-2.5 are characterized by high concentration of short-chain alkanes (<C22),
349 especially the even-terms (C16, C18, C20) and by CPI values lower than 3 (see Table 1a). From
350 literature it is well known that n-alkanes with low and medium chain length (<C25) mainly come
351 from fossil fuel combustion (Duan et al., 2010). In particular, Rogge et al. (1993a) found that
352 particle-phase n-alkanes <C19 should be contributed from unburned gasoline and from diesel
353 engine.

354 The n-alkanes content and CPI values of MXS and CTS indicate their anthropogenic origin,
355 however the calculated indexes do not clearly suggest further hypothesis on the sources. The lowest
356 n-alkanes content in CAS and MND together with their higher contribution from light homologues
357 (C16, C18, C20) and low CPIs values (<2) indicate that the n-alkanes sources are mainly anthropic
358 and they impact CAS and MND less than the other sites of the domain.

359 Regarding PM_1 samples, the CPIs indicate a dominance of anthropic sources in the finest fractions
360 of all the sites (see Table 1a). As above mentioned, the sum of all n-alkanes measured in MXD-1
361 accounts for about 100% of that in the respective $PM_{2.5}$, indicating a preferential partition of these
362 organic compounds in the finest PM fraction, as usually observed in areas strongly impacted by
363 anthropic sources (Aceves and Grimalt, 1993).

364

365 **3.1.2 n-alkanes in winter**

366 In winter, the highest content of alkanes was measured in the suburban, the rural and the urban sites,
367 CAS, MND and MGA, respectively (see Fig. 2d). In particular, CAS and MND are characterized by

368 high concentrations of long-chain homologues (>C₂₅). These compounds typically come from plant
369 wax or from biogenic fuel burnings (Li et al., 2010; Simoneit et al., 1991). The low values of CPI₂₅₋
370 ₃₂ of CAS and MND indicate that in these sites long-chain alkanes have mainly pyrogenic origin
371 rather than biogenic (Górka et al., 2014). CAS is characterized by high PM₁₀ concentration coming
372 from wood heating of the semi-rural suburban area, as demonstrated by specific high resolution
373 information about different heating fuels (natural gas, LPG and wood) (Rossi et al., 2012). MND
374 station is located in a rural area with low density of population, but the sampler was placed under
375 the influence of a domestic biomass combustion source emission not recognized during the
376 monitoring planning. For this reason, MND was considered not representative of the averaged
377 environment characteristics of the area in which it is located. The high concentration of alkanes
378 detected during the cold season in MND could thus derive from its peculiar location.

379 On the contrary the urban site (MGA) should not be impacted by wood combustion, due to the high
380 percentage of natural-gas-fuelled domestic heaters, therefore other sources must be considered.
381 From Table 1b, it can be seen that on one hand the CPI₂₅₋₃₂ of MGA is the highest one (>3) and it
382 suggests biogenic sources and, on the other hand, the %WNA and CPI₁₅₋₃₂ are low, indicating
383 anthropogenic emissions. These two apparently contradictory aspects indicate a mixed contribution,
384 with different weights, from anthropic sources (short-chain homologues) and biogenic ones (long-
385 chain homologues).

386 The highest concentration of n-alkanes in PM_{2.5} was found in MXW with respect to all the other
387 sites (i.e. MXW, CTS, CTW, MXD, MXS) (see Fig. 2d). The CPIs in Table 2b show that alkanes in
388 PM_{2.5} collected at MXW derive from both natural and anthropic sources, and the second ones seems
389 to prevail. MXD, despite the choice of being representative of the most polluted area in the domain,
390 exhibits a low content of n-alkanes in PM_{2.5}; this is not in contradiction to the choice of the location
391 of this sampling site, because it is well known that n-alkanes sources emissions are very different
392 either in composition and in quantity and, first of all, not only related to pollutant sources.

393 To investigate about the partition of n-alkanes on different fractions of atmospheric aerosol, the
394 concentrations were normalized by the amount of particulate in the stations where both PM_{2.5} and
395 PM₁ fractions were sampled (i.e. MXW, CTW and MXD). In winter MXW-1 and, to a lesser extent,
396 MXD-1 showed higher alkanes normalized concentrations than their respective PM_{2.5} (i.e. MXW-
397 2.5 and MXD-2.5). This finding indicates that these compounds are preferentially associated to the
398 finest fraction of PM, according to literature data (Bi et al., 2005; Pietrogrande et al., 2010). Indeed,
399 the ΣC_{14-C32} in PM₁ accounts for about 100%, 40% and 75% of that in PM_{2.5} in MXW, CTW and
400 MXD, respectively. Furthermore, all the CPI values of PM₁ samples are generally less than or equal
401 to that of the respective PM_{2.5} samples (see MXW and CTW in Table 1b), further confirming the

402 increasing contribution of anthropogenic alkanes with decreasing of PM size (Alves et al., 2000;
403 Aceves and Grimalt, 1993).

404

405 **3.2 PAHs**

406 As briefly mentioned in the Introduction, PAHs occur in the atmosphere as complex mixtures of
407 congeners with different molecular weights: lighter PAHs (with 2-3 aromatic rings) were found
408 preferentially in the vapor-phase, whereas PAHs with higher molecular weight (with 4-6 aromatic
409 rings) were found almost totally adsorbed on the particulate matter (Masiol et al., 2012; Chrysikou
410 and Samara, 2009). Therefore the lighter congeners in PM could be not representative of their total
411 amount in the air, nonetheless they were included in the present study, as already done in other
412 recent works dealing with the composition of particulate matter (Souza et al., 2014; Kong et al.,
413 2010; Cvetković et al., 2015).

414 As shown in Figure 3, PAHs amounts are generally higher of one order of magnitude in winter than
415 in summer; this finding was also observed in other studies carried out in Italy (Masiol et al., 2012 in
416 Venice, Cincinelli et al., 2007 in Prato). The abbreviations used to indicate PAHs are reported in
417 Table S3.

418

419 **FIG 3**

420

421 The higher PAHs concentrations in winter than in summer can be due to both an increase in
422 emissions from heating systems (e.g. fossil fuel and wood combustion) and meteorological factors
423 (Cincinelli et al., 2007). Regarding this last aspect, PAHs in PM increases going from summer to
424 winter because of several factors, such as the lowering of H_{mix} that limits pollutants dispersion, a
425 less effective photo-induced degradation of PAHs (following a lower intensity of solar radiation)
426 and, finally, more favourable gas-to-particle partition ratios at lower temperatures (Terzi and
427 Samara, 2004) (see Paragraph 2.4 and Table S1).

428 In detail, the sum of detected PAHs in summer is 0.44 ng m^{-3} in $\text{PM}_{2.5}$ and 0.40 ng m^{-3} in PM_1 ,
429 equivalent to $22.3 \text{ } \mu\text{g g}^{-1}$ and $25.7 \text{ } \mu\text{g g}^{-1}$ of $\text{PM}_{2.5}$ and PM_1 respectively. In winter, the sum of PAHs
430 is 6.3 ng m^{-3} in $\text{PM}_{2.5}$ and 5.7 ng m^{-3} in PM_1 and corresponds to $186 \text{ } \mu\text{g g}^{-1}$ of $\text{PM}_{2.5}$ and $253 \text{ } \mu\text{g g}^{-1}$
431 of PM_1 . These concentrations of PAHs are similar to those measured in other studies on $\text{PM}_{2.5}$
432 collected in the Po Valley (Pietrogrande et al., 2015, Perrone et al., 2012).

433 By considering that PM_1 constitutes a high percentage of $\text{PM}_{2.5}$ (see Paragraph 3), it can be deduced
434 that PAHs mainly accumulated in PM_1 in both seasons. This is in agreement with studies conducted
435 elsewhere (Bi et al., 2005, Allen et al., 1996, Alves et al., 2000) which report that PAHs are mainly

436 associated (60–90%) with the fine aerosol fraction. This preferred partition could derive from the
437 higher adsorption of PAHs on the finest particles surface, due to their higher total surface area and
438 lower water content (lower polarity) with respect to coarser particles (Allen et al., 1996). In
439 addition, the dominance of PAHs in the smallest fraction is consistent with combustion processes as
440 a major source of these particles (Crimmins, 2006; Masiol et al., 2012)
441 In winter, the sum of the concentrations of the isomers benzo[b]fluoranthene and
442 benzo[j]fluoranthene (i.e. BbjF) has the largest dispersion with highest median value, as shown in
443 Fig. 3b. These PAHs were found to be ones of the most abundant also in Baltimora (US) during
444 Supersite investigations (Crimmins, 2006). In particular, the isomer benzo[b]fluoranthene was
445 indicated as one of the marker of diesel-powered vehicles by Harrison et al. (1996). In Fig. 3b it can
446 be also observed that in the cold season, high-molecular weight PAHs are the most abundant class,
447 indeed 5-rings compounds account for almost 50% and 5- to 6-rings compounds account for almost
448 70% of all PAHs. Such distribution profiles could indicate that the major emission sources in
449 wintertime are wood combustion and traffic, in agreement with other studies carried out in Northern
450 Italy (Perrone et al., 2012; Vassura et al., 2014). In the following (see Paragraph 3.4), spatial and
451 season variations of PAHs are discussed.

452

453 **3.3 Nitro-PAHs**

454 The concentrations of nitro-derivatives above the detection limits were scarce, however it was
455 possible to make some qualitative observations. From the few data available, the sum of detected
456 nitro-PAHs in summer is 0.12 ng m^{-3} in $\text{PM}_{2.5}$ and 0.044 ng m^{-3} in PM_1 and corresponds to $6.25 \mu\text{g g}^{-1}$
457 of $\text{PM}_{2.5}$ and $2.82 \mu\text{g g}^{-1}$ of PM_1 . In winter, the sum of nitro-PAHs is 0.050 ng m^{-3} in $\text{PM}_{2.5}$ and
458 0.015 ng m^{-3} in PM_1 and corresponds to $1.49 \mu\text{g g}^{-1}$ of $\text{PM}_{2.5}$ and $0.668 \mu\text{g g}^{-1}$ of PM_1 .

459 Unlike PAHs whose higher levels were observed during winter, nitro-PAHs concentrations were
460 generally higher during the summer. This has been observed also in the Los Angeles basin by
461 Reisen and Arey (Reisen and Arey, 2005) and can indicate that the origin of these nitro-derivatives
462 in summer is mainly due to secondary processes.

463 Nitro-PAHs in PM_1 were about 30% (winter) and 36% (summer) of those found in $\text{PM}_{2.5}$. However,
464 by considering only sites where both PM_1 and $\text{PM}_{2.5}$ were sampled (i.e. MXW, CTW and MXD),
465 the above percentages seem to be significantly different. In fact, in winter 88% of nitro-PAHs are
466 concentrated into the finest fraction, while in summer this percentage is reduced to only 18%. A
467 similar trend in the partition of nitro-PAHs during the cold and hot season has been also observed
468 by Albinet et al. (2008), who report about larger nitro-PAHs values in super micrometer ($> 1.3 \mu\text{m}$)
469 aerosol fraction in summer than in winter. In that work, it was proposed that the difference of

470 chemical affinities of the organic compounds with the super micrometer fraction of the aerosol
471 could be responsible for the differences of size distributions of the nitro-PAHs. Another possible
472 explanation has been proposed by Cecinato et al. (1999). Following these authors, heterogeneous
473 reactions leading to secondary nitro-PAHs preferentially occur on coarser particles, due to the
474 presence therein of metal oxides or salts acting as catalysers of such reactions. Both hypotheses
475 could explain the observed trend. Based on these observations, the origin of nitro-PAHs in PM
476 cannot be precisely attributed so that secondary origin of nitro-derivatives cannot be excluded.

477 In Figure 4, the nitro-PAHs concentrations in the sampling sites averaged on each campaign are
478 shown.

479

480 **FIG 4**

481

482 The highest total nitro-PAHs content was detected in MXW-2.5 in summer, while in MXS and in
483 its control CTS in winter. It should be considered that the most abundant nitro-derivative in summer
484 is 1-nitropyrene (see Fig. 4a) as observed also by Tang et al. (2005). It is known from literature that
485 1-nitropyrene is the dominant nitro-PAH found in diesel exhausts (Crimmins, 2006; Bamford et al.,
486 2003), but it can be detected also in gasoline engines emissions, even if at lower concentrations than
487 diesel engines (WHO, 2003). Therefore, this compound seems derive from vehicular traffic.
488 However 9-nitrophenanthrene, which was significantly detected in MXW-2.5, can be ascribed to
489 biomass combustion other than vehicular emissions as recently proposed by Souza et al. (2014).
490 This finding confirms that biomass combustion is one important source of organics in MXW-2.5 as
491 previously discussed for n-alkanes (see Paragraph 3.1).

492 In winter, 9-nitrophenanthrene and 1-nitropyrene were the most abundant nitro-PAHs (see Fig. 4b).
493 In this season, relevant concentrations of 1-nitropyrene were found in the urban and the rural site,
494 MGA and MND, respectively. For what concerns MGA, the vehicular traffic could be the principal
495 source of this nitro-derivative, which tends to accumulate in the low atmosphere due to inefficient
496 mixing in the air column in the cold season (Stracquadiano et al., 2007). MND is located in a rural
497 area, however, as previously discussed in Paragraph 3.1.2, the sampling station was located near a
498 house where a stove burning pellets was employed for domestic heating, therefore it can be inferred
499 that nitro-PAHs detected in this site can derive from biomass combustion. At this purpose, some
500 studies (Shen et al., 2012; WHO, 2003) indicated residential heating and wood burning as sources
501 of nitro-PAHs, among which 1-nitropyrene.

502 In winter, CTS and MXS are characterized by a high 9-nitrophenanthrene concentration possibly
503 due to biomass or industrial combustion processes.

504 3.4 PAHs seasonal and spatial distribution

505 Principal Components Analysis (PCA) and cluster analysis were performed on average chemical
506 compositional data obtained from the two campaigns separately (ng m^{-3}) divided by the particulate
507 matter concentration ($\mu\text{g m}^{-3}$) to obtain data in $\text{ng } \mu\text{g}^{-1}$ unit.

508 PCA was performed for the summer campaign by selecting only 13 PAHs, because data
509 concentrations of other analytes were below the LOD in more than 70% of cases. Figure 5 shows
510 the scores of PAHs for PM sampled during summer and the variable loadings in the space of the
511 first three Principal Components, which explain for 89.7% of the total variance. In particular, PC1
512 accounts for 69.8%, PC2 for 14.3% and PC3 for 5.6%.

513

514 FIG 5

515

516 PC1 accounts for differences in the total amount of PAHs since its variables loadings are very
517 similar from each other. The average normalized concentrations of PAHs are higher for CTS and
518 MXD (having lower PC1 scores) and, in particular, PAHs amount in the finest fraction of MXD is
519 higher than what measured in the coarser fraction, similarly to what observed for n-alkanes (see
520 Paragraph 3.1). The high PAHs content and their preferential partition into PM_1 suggest a relevant
521 contribution of anthropic combustion sources impacting this site (Cecinato et al., 1999; Crimmins,
522 2006), thus confirming that MXD represents a maximum of the domain as determined by the
523 preliminary simulation study. Scores of MND and MGA on PC1 indicate that these sites contain
524 relative lower amount of PAHs: also in this case this finding well agrees with the simulation study
525 of emissions in the domain.

526 On PC2, low-molecular weight PAHs (especially naphtalene) have negative loadings, while
527 benzo[g,h,i]perylene and indeno[1,2,3-cd]pyrene have high positive loadings. PC2 well
528 discriminates MXD and CTS. In detail, MXD is characterized by high concentrations of low-
529 molecular weight PAHs, which could be emitted by heavy-duty diesel vehicles (Ravindra et al.,
530 2008). This site is indeed near freeways and railroads, hence characterized by high traffic. The high
531 positive score of CTS on PC2 indicates concentrations higher than the average of
532 benzo[g,h,i]perylene and indeno[1,2,3-cd]pyrene, mainly due to vehicles emissions. The attribution
533 of a specific source of vehicular emission (i.e. gasoline- or diesel- fuelled vehicles) is difficult, since
534 some studies report that emissions profiles of gasoline and diesel exhausts are rather similar
535 (Harrison et al., 1996; Crimmins, 2006), while other works (Omar et al., 2002; Rinehart et al., 2006)
536 indicate that higher molecular weight PAHs are mainly related to gasoline-fuelled vehicles. The
537 average composition of PM_1 in MXW and CTW is slightly enriched in low molecular weight PAHs

538 with respect to PM_{2.5}. No differences were observed for the winter maximum MXW-2.5 and its
539 control CTW-2.5, while the summer maximum MXS and its control CTS belong to different
540 clusters. In addition to higher total content of PAHs than the average, the PM sampled in CTS is
541 strongly enriched in anthracene and, to a lesser extent, in benzo[k]fluoranthene (high positive
542 loading on PC3). The INP/BghiP ratio (see Table S5), which is the highest among all sites, together
543 with concentrations of benzo[k]fluoranthene higher than the average suggest that CTS is impacted
544 by diesel-fuelled vehicles emissions (Harrison et al., 1996), in addition to gasoline-fuelled ones (see
545 PAHs diagnostic ratios in Supplementary Information).

546 In order to highlight possible seasonal variations, the PCA for the winter campaign was performed
547 on the same 13 PAHs considered in the previous elaboration (see Figure 6). PC1 accounts for
548 47.9%, PC2 for 27.5% and PC3 for 14.4% of the total variance.

549

550 **FIG 6**

551

552 In CTW-2.5 and MXW-1 the content of PAHs is higher than the average, as indicated by the large
553 scores on PC1 (Fig. 6). This is also valid for CTW-1 and MXD-1, even if to a lesser extent.
554 Therefore, in the cold season, higher concentrations than the average were observed in all the PM₁
555 samples, while in summer this was true only for MXD-1. This can be due to the increase of
556 combustion sources in winter with respect of summer (Ravindra et al., 2006; Chrysikou and
557 Samara, 2009; Allen et al., 1996).

558 To acquire indications about these possible sources, the other PCs were considered. MXW-1 is well
559 separated from other PM₁ samples by PC2. On this PC, fluoranthene, pyrene and benzo[a]pyrene
560 have high negative loadings. Hence, the PM sampled in MXW-1 is particularly enriched of these 3
561 analytes, whose levels are comparable to what measured in some PM_{2.5} samples (i.e. MGA, CTS
562 and CTW-2.5). On the contrary, in CTW-1 and MXD-1 lower concentrations of fluoranthene,
563 pyrene and benzo[a]pyrene than the average were measured.

564 Pyrene and fluoranthene have been identified to have reasonably high levels in emissions from
565 several sources such as wood combustion, oil burning, industrial emissions, gasoline and diesel-
566 powered vehicles, incineration (Ravindra et al., 2008; Cincinelli et al., 2007; Harrison et al., 1996).

567 However, in the coarser fraction collected in MXW (i.e. PM_{2.5}) the relative concentrations of pyrene
568 and fluoranthene do not significantly differ from those of other sites.

569 The lowest total levels of PAHs were measured in MXS.

570 PCA analysis on winter campaign was then performed by including 5 further analytes (i.e.
571 cyclopenta[cd]pyrene, dibenzo[a,c+a,h]anthracene, dibenzo[a,l]pyrene, dibenzo[a,e]fluoranthene

572 and dibenzo[a,e]pyrene) to the above-mentioned 13. This wasn't carried out in summer because
573 concentration data of these additional PAHs were below the LOD in most cases. In fact, in summer
574 concentrations lower of one order of magnitude than in winter were measured (see Fig. 3).

575 The PCA based on winter data of 18 PAHs didn't show relevant changes with respect of the
576 previous statistical analysis, except that CTW-2.5 and MXW-1 have been split in two different
577 clusters, well separated by PC3. In detail, CTW-2.5 was characterized by concentrations of
578 naphthalene, anthracene, dibenzo[a,c+a,h]anthracene, dibenzo[a,e]fluoranthene and
579 dibenzo[a,e]pyrene higher than the average. One of the possible sources of these compounds can be
580 vehicles emissions: low-molecular weight PAHs (naphthalene and anthracene) could derive from
581 diesel exhausts while high-molecular weight PAHs (dibenzo[a,c+a,h]anthracene and
582 dibenzo[a,e]pyrene) can be ascribed to gasoline-fuelled vehicles (Ravindra et al., 2008).

583 The particulate sampled in MXW-1 was particularly rich in benzo[b+j]fluoranthene. These
584 compounds, in addition to pyrene and fluoranthene, were found in emissions from diesel-fuelled
585 vehicles (Ravindra et al., 2006).

586

587 **4. Conclusions**

588 In this study the concentrations of n-alkanes in the range C₁₄-C₃₂, PAHs and nitro-PAHs were
589 measured in PM_{2.5} and PM₁ collected at 8 sampling sites around a municipal waste incinerator
590 located near Bologna, in Emilia Romagna region (Northern Italy). The analysis of PM composition
591 over the studied domain has been accomplished to investigate the similarities and differences
592 between the various monitoring stations. This is the first step to bring out any evidence of impact of
593 the different and peculiar local pollutant sources, like, for example, an incinerator plant. It was not
594 possible clearly identify the contribution of the emissions of the incinerator itself in the domain, by
595 analysing the selected organic compounds in PM. Nonetheless, some interesting findings have been
596 pointed out. In particular, the PAHs concentrations in PM are higher of one order of magnitude in
597 winter than in summer. Similarly, n-alkanes showed higher concentrations in the cold season even if
598 the difference with respect to summer is smaller than PAHs. On the contrary, nitro-PAHs
599 concentration in PM increases in hot season.

600 In both campaign, high concentrations of short-chain alkanes, which are typically emitted by
601 anthropic sources, have been measured in the maximum of the domain and in the urban site (i.e.
602 MXD and MGA, respectively), indicating the impact of vehicular emissions on PM compositions.

603 The results also showed that PAHs accumulate on the finest fraction of aerosol, especially in winter,
604 while in summer nitro-PAHs are preferentially partitioned on the PM_{2.5}

605 The highest total nitro-PAHs content was detected in summer in MXW-2.5 and in MXS and its
606 control CTS in winter.

607 Principal Components Analysis was performed on PAHs concentrations normalized by the PM
608 amount. In summer, concentrations higher than the average were found in MXD, especially in the
609 finest fraction of aerosol (i.e. MXD-1). This finding suggests a strong contribution of anthropic
610 combustion sources, especially vehicular traffic, as it was expected due the location of this station.
611 No significant differences were observed between MXW-2.5 and its control CTW-2.5, while MXS
612 and its control CTS belong to different clusters.

613 In winter, in MXW-1 samples, the concentrations of pyrene, fluoranthene and
614 benzo[b+j]fluoranthene higher than the average could be ascribed both to waste incineration and to
615 diesel-powered vehicles.

616 PAHs and n-alkanes showed the highest concentrations in the same PM₁ samples and in particular
617 MXD-1 in summer and MXW-1 in winter.

618

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624

625 **Appendix A. Supplementary data**

626 Supplementary data related to this article are included.

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876 **FIGURE CAPTIONS**

877

878 Figure 1: Monitoring stations locations

879

880 Figure 2: Box plot of mean concentrations of n-alkanes measured a) in summer and b) in winter; n-
881 alkanes mean composition in the sampling stations c) in summer and d) in winter.

882

883 Figure 3: Box plot of mean concentrations of PAHs a) in summer and b) in winter. For PAHs
884 abbreviations, see Table S3 in Supplementary Information.

885

886 Figure 4: Concentrations of nitro-PAHs in PM collected in the sampling stations averaged on the
887 campaign duration, a) summer and b) winter

888

889 Figure 5: Score and loading plots of the first three PCs based on the selected PAHs, for the summer
890 campaign (data normalized). For PAHs abbreviations, see Table S3 in Supplementary Information.

891

892 Figure 6: Score and loading plots of the first three PCs based on the selected PAHs, for the winter
893 campaign (data normalized). For PAHs abbreviations, see Table S3 in Supplementary Information.

Table 1: C_{max}, CPI indexes and %WNA for n-alkanes a) in summer and b) in winter

a)

Site	C _{max}	CPI ₁₅₋₃₂	CPI ₂₅₋₃₂	CPI ₁₄₋₂₅	%WNA
MXW-1	C16	0.54	2.14	0.17	45
MXW-2.5	C29	1.03	1.15	0.78	26
CAS	C16	0.60	1.61	0.25	31
CTS	C29	1.08	1.67	0.44	35
CTW-1	C16	0.47	1.33	0.25	14
CTW-2.5	C29	1.96	3.30	0.67	48
MGA	C18	0.45	2.21	0.18	31
MND	C18	0.43	2.53	0.22	33
MXD-1	C18	0.56	1.42	0.29	16
MXD-2.5	C18	0.42	1.98	0.19	23
MXS	C29	1.14	2.08	0.38	34

b)

Site	C _{max}	CPI ₁₅₋₃₂	CPI ₂₅₋₃₂	CPI ₁₄₋₂₅	%WNA
MXW-1	C29	1.19	1.18	1.25	9
MXW-2.5	C29	1.26	1.16	2.23	33
CAS	C28	0.89	0.83	0.19	2
CTS	C23	1.45	1.47	1.53	23
CTW-1	C29	1.17	1.50	1.03	11
CTW-2.5	C29	1.35	1.28	1.90	33
MGA	C17	0.89	3.65	0.75	27
MND	C29	1.13	1.07	2.00	18
MXD-1	C29	1.80	1.80	1.87	24
MXD-2.5	C27	1.36	1.84	1.10	24
MXS	C17	1.75	2.45	1.45	27

Figure 1
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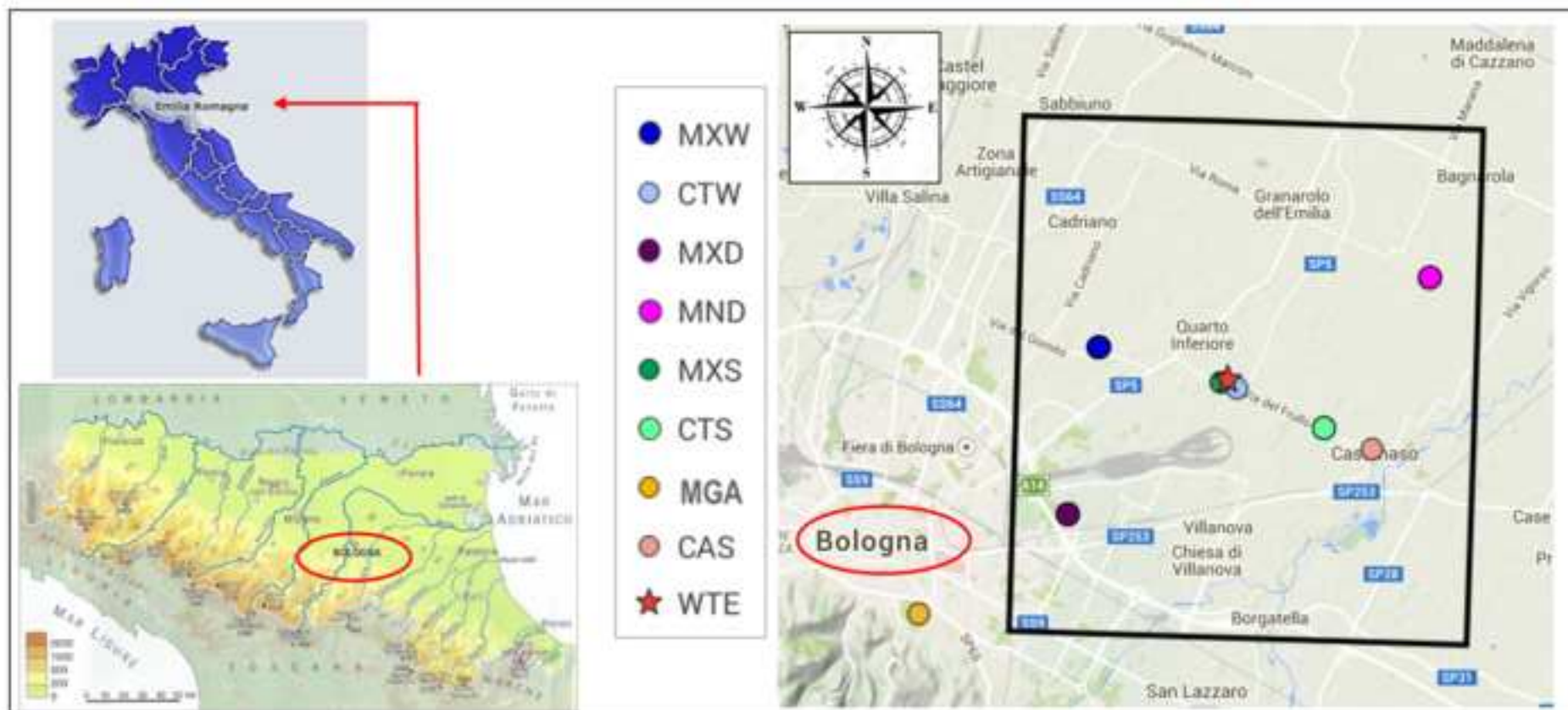


Fig 1

Figure 2
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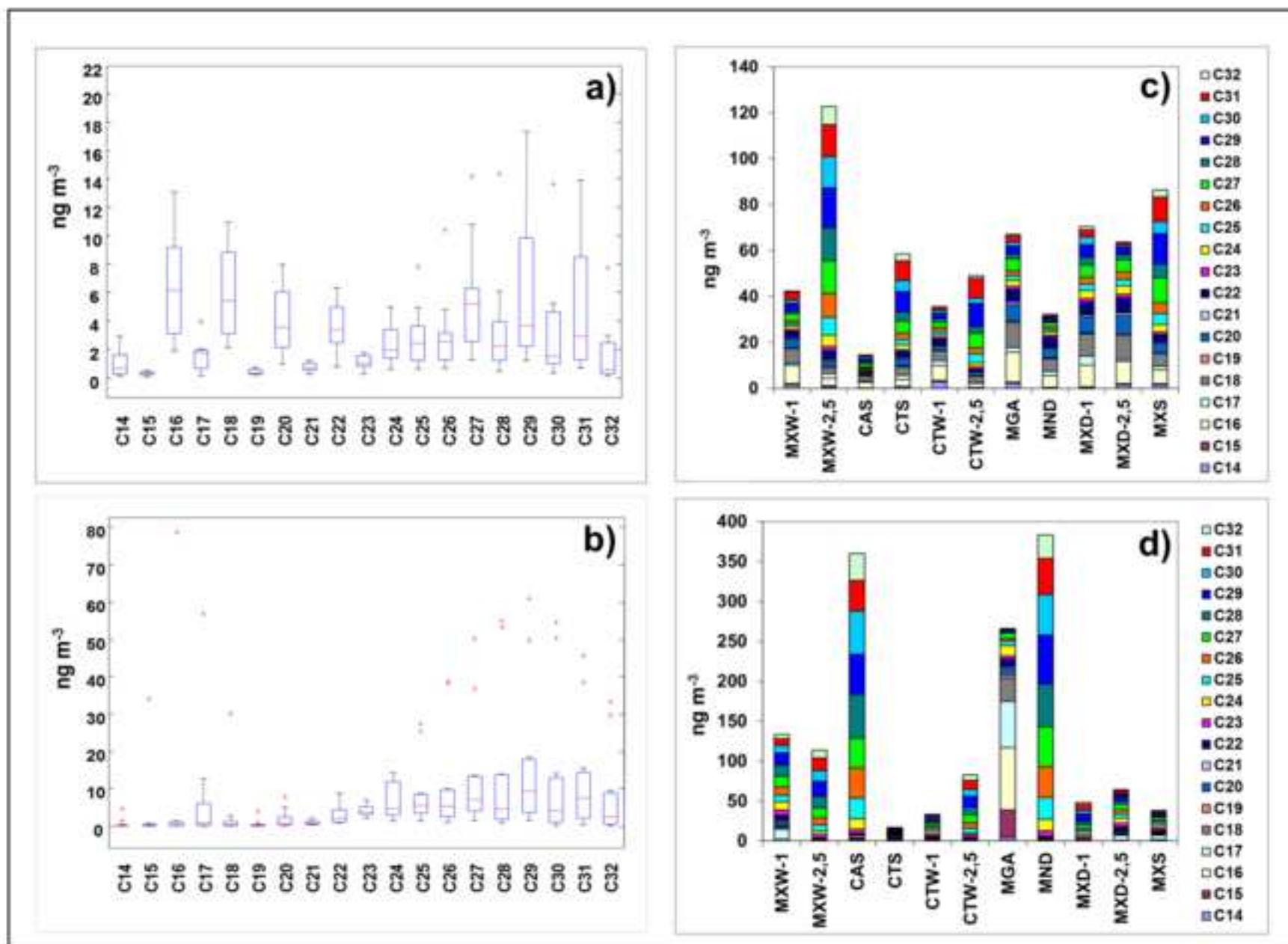


Fig 2

Figure 3

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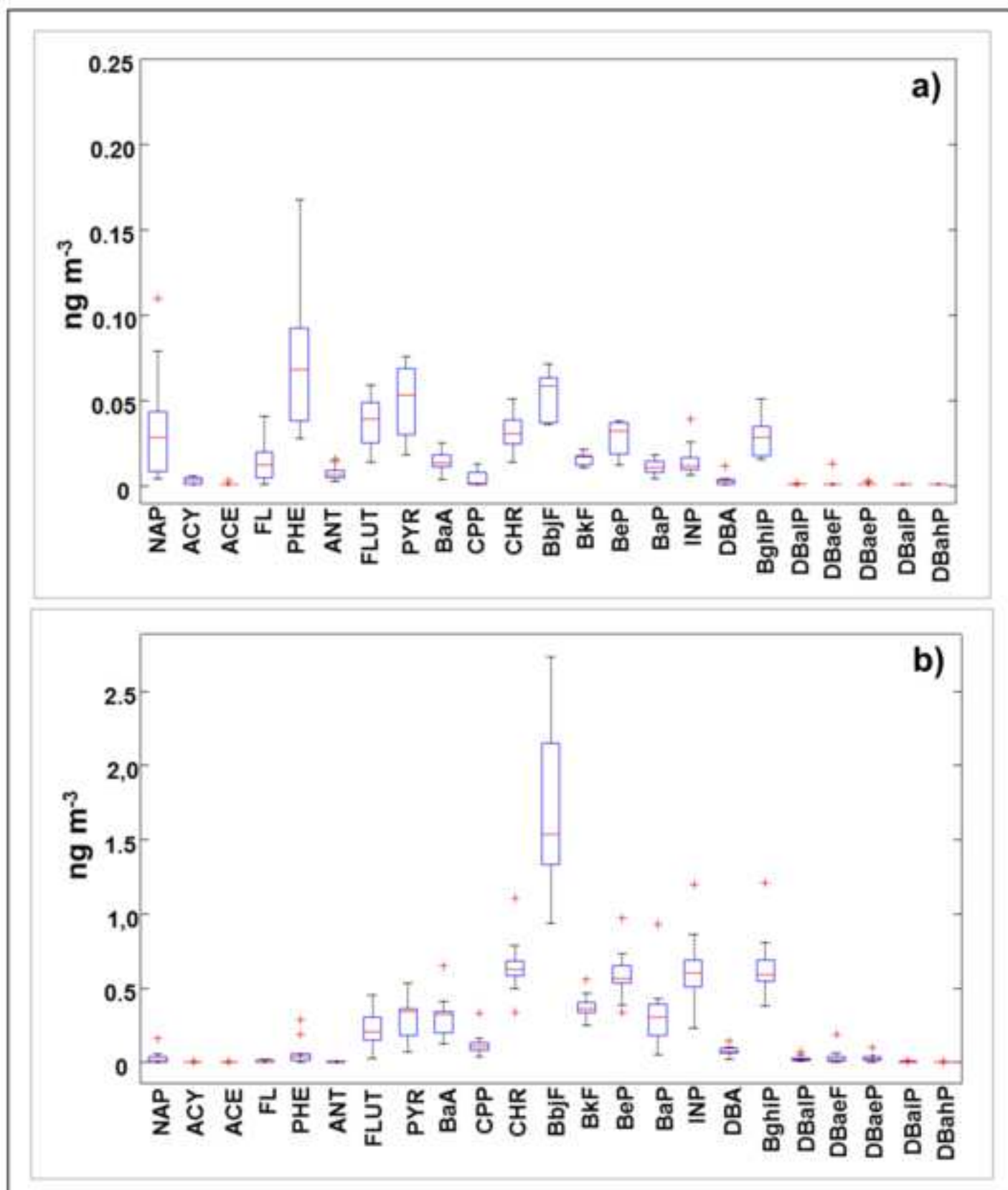


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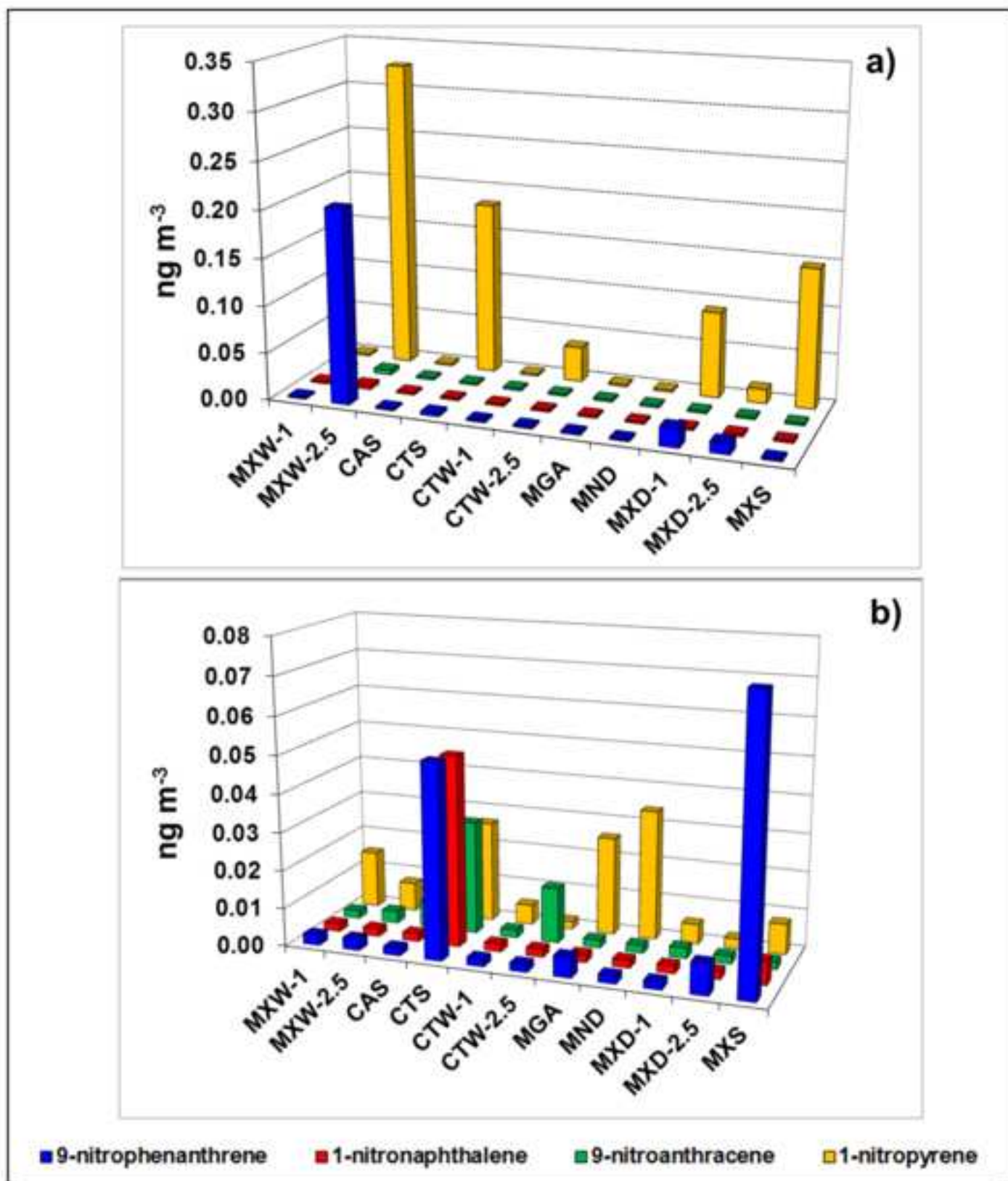


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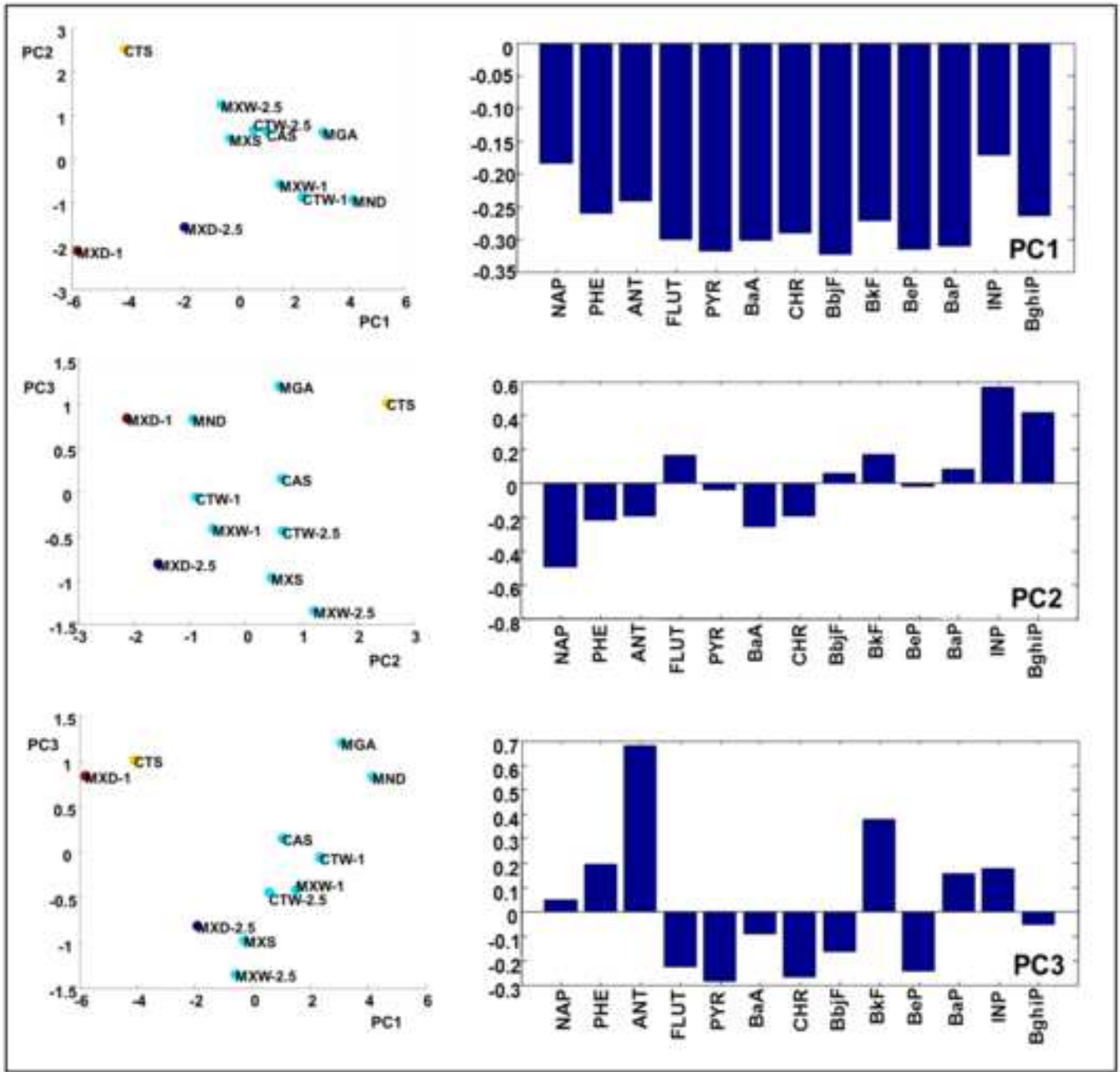


Fig 5

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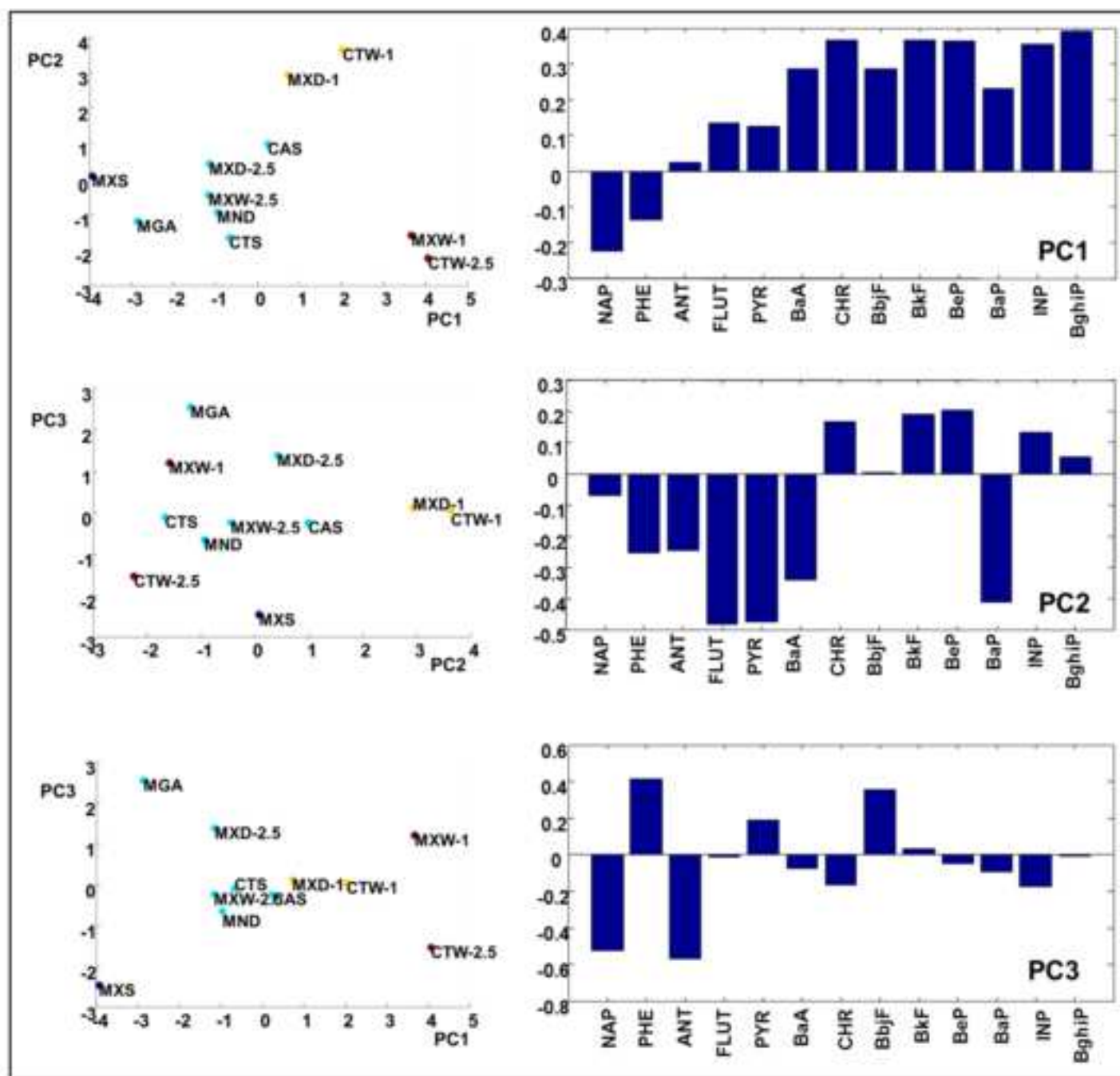


Fig 6

Highlights

- $PM_{2.5}$ and PM_1 were sampled in different sites close to a municipal waste incinerator
- n-alkanes, PAHs and nitro-PAHs were determined in both PM collected fractions
- Higher concentrations of PAHs and n-alkanes were measured in winter than in summer

Supplementary Material

[Click here to download Supplementary Material: SUPPLEMENTARY INFORMATION_revised.docx](#)