Title: Determination of n-alkanes, PAHs and nitro-PAHs in PM\(_{2.5}\) and PM\(_1\) sampled in the surroundings of a municipal waste incinerator

Article Type: Research Paper

Keywords: PM\(_{2.5}\); PM\(_1\); n-alkanes; PAHs; nitro-PAHs; incinerator plant

Abstract: This work investigates n-alkanes in the range C\(_{14}\)-C\(_{32}\), polycyclic aromatic hydrocarbons (PAHs) and nitrated PAHs (nitro-PAHs) composition of PM\(_{2.5}\) and PM\(_1\) 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 km\(^2\) 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 PM\(_1\) 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 (>C\(_{27}\)) 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, PM\(_1\) was enriched in PAHs in the site close to the incinerator with respect to its control.
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

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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 PM2.5 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:


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:


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 μg g⁻¹ at p. 13 lines 429-431 and at p. 14 lines 456-458.
Determination of n-alkanes, PAHs and nitro-PAHs in PM$_{2.5}$ and PM$_1$ sampled in the surroundings of a municipal waste incinerator

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Abstract

This work investigates n-alkanes in the range C14-C32, polycyclic aromatic hydrocarbons (PAHs) and nitrat ed PAHs (nitro-PAHs) composition of PM$_{2.5}$ and PM$_1$ 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 km$^2$ 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 PM$_1$ 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, PM$_1$ was enriched in PAHs in the site close to the incinerator with respect to its control.

Keywords

PM$_{2.5}$; PM$_1$; n-alkanes; PAHs; nitro-PAHs; incinerator plant

1. Introduction

The incineration process can result in three potential sources of exposure: emissions to the atmosphere, solid ash residues and cooling water. Provided that solid ash residues and cooling water are appropriately handled and disposed of, atmospheric emissions remain the only significant route of exposure to people. The combustion gives rise to fine particles that can have negative effect on human health due to their size and composition (Laden et al., 2000; Morawska and Zhang, 2002). In particular, during incomplete combustion of fossil fuels and biomass, polycyclic aromatic
hydrocarbons (PAHs) can be released into the atmosphere (Jedynska et al., 2014), partitioned between the vapour phase and the particle matter (the partition coefficient strongly depends on the PAH molecular weight) (Masiol et al., 2012; Cvetković et al., 2015). These compounds are of great concerns: the United States-Environmental Protection Agency (US-EPA) classified 16 PAHs as priority pollutants based on toxicity, potential for human exposure, frequency of occurrence at hazardous waste sites and the extent of available information (EPA, 2014). Among these 16 PAHs, US-EPA considers 7 (i.e. benzo[a]anthracene, chrysene, benzo[a]pyrene, benzo[b]fluoranthene, benzo[k]fluoranthene, dibenz[a,h]anthracene, and indeno[1,2,3-cd]pyrene) as probable human carcinogens (EPA, 2014).

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

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

Because of the possible presence of these contaminants in the incinerator emissions and of their toxicity, there is a high perception of health risk, especially for people living nearby these plants. Although this is a very felt issue, many studies state that “modern, well managed incinerators make only a small contribution to local concentrations of air pollutants. It is possible that such small additions could have an impact on health but such effects, if they exist, are likely to be very small and not detectable” (HPA, 2009). However, it should also be considered that location, meteorological conditions and plant characteristics can play an important role on the emissions characteristics. Moreover, in the literature the works concerning the PAHs and nitro-PAHs composition of PM collected in area close to an incinerator are relatively scarce, especially in Italy, and only few of them deal with PM$_1$, which is generally known as harmful for human health (Chen et al., 2016). In order to acquire new knowledge about the air quality in the proximity of incinerators, the local Emilia Romagna (ER) Administration promoted a wide research project called MONITER (http://www.arpae.it/moniter/). In particular this work, which is a part of the MONITER project, reports the content of PAHs and nitro-PAHs in PM$_1$ and PM$_{2.5}$ collected in the neighbourhood of a Municipal Waste to Energy Incinerator (WTE) located in the ER region. Additionally, to differentiate the potential sources of these contaminants, the composition in n-
alkanes of the particulate was also evaluated. It is well known that n-alkanes can be emitted from anthropic or natural (mostly vegetal) sources and, for this reason, they are considered useful in tracking the origin of atmospheric aerosol (Simoneit, 1989; Duan et al., 2010). In particular, the abundance distribution of the odd/even terms is a key diagnostic parameter in discriminating between the biogenic and anthropogenic nature of n-alkanes sources (Pietrogrande et al., 2010).

The aim of this work is to evaluate the effect of a WTE on PM composition by comparing the concentrations of organic compounds (i.e. n-alkanes, PAHs and nitro-PAHs) in the aerosol collected at different sites in a domain of about 10 km² around WTE location, in two different seasons.

2. Materials and Methods

2.1 Sampling of particulate matter

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

A preliminary study with ADMS–Urban (Cerc, Cambridge, UK) dispersion model was performed to select the coordinates of incinerator maximum impact and the related control sites, evaluating PM₁₀ and NOₓ emissions as pollutant tracers. ADMS simulations were used with the aim to maximize prospective gravimetric differences of coupled max and control sites, not to modelling air quality over the domain. Background concentrations (i.e. due to emissions not included in the domain) have been assumed uniform in the domain and not modelled. Further details of the procedure are described elsewhere (Rossi et al., 2012; Bonafè and Rossi, 2011). The remaining sites were chosen using the diffusion maps as a qualitative guide, under the same hypothesis and limitations above described.

Seven out of eight monitoring stations were placed in a domain of 8x9 km² around the plant; the eighth station (MGA) was located inside the urban area of Bologna, in a site used for urban background measurements by ARPAE-ER (Emilia Romagna - Regional Agency for Prevention, Environment and Energy). The seven monitoring stations inside the domain were chosen based on the following criteria:
• MXW is representative of the maximum impact of plant emissions, in terms of concentration at the ground level, in the meteorological winter conditions.

• CTW is selected as follows:
  i) the estimated impact of the relevant confounding emissions included in the domain should be similar to MXW (with a tolerance of +/-25%);
  ii) the estimated impact of the incinerator should be minimum.

Therefore, CTW is used as a "control" of MXW.

• MXS was chosen as MXW but in the meteorological summer conditions.

• CTS was chosen as a “control” of MXS, with the same criteria as CTW.

• MXD represents the most polluted site of the domain.

• MND is surrounded by agricultural land, so it represents a rural area of the domain.

• CAS is located in a suburban area.

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

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

**FIG 1**

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

PM$_1$ samples were collected solely in MXW, MXD and CTW sites and are notated as MXW-1, MXD-1 and CTW-1, respectively. The PM$_{2.5}$ samples collected in the above-mentioned three sites are notated as MXW-2.5, MXD-2.5 and CTW-2.5. For all the other sites (e.g., CAS, CTS, MGA, MND, and MXS), only PM$_{2.5}$ was sampled.

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

For each sampler, except MXW-2.5, chemical analyses were performed by using filters from two consecutive days (analysis on 48h time basis). A quarter of filter of one day was pooled together with a quarter of a filter of the subsequent day (Sarti et al., 2015) before analysis. For MXW-2.5 chemical analyses were performed on 24h time basis. In this case, two coupled samplers have been used and the two filters of the same day underwent to the same procedure above described. The
frequency of analysis of MXW-2.5 was increased since simulations indicated this site as representative of maximum deposition of plant emissions, under averaged meteorological conditions (Rossi et al., 2012). The choice of combining two filters together derives from the necessity of performing chemical analyses on a wide number of analytes by several laboratories. In this work, the mean values of every pollutant over the same periods of time were compared for all the sampling sites.

2.2 Analytical procedure

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

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

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

The n-alkanes analysis was performed under the following temperature program: (1) temperature ramp from 60 °C to 300 °C at 10 °C min⁻¹, (2) 300 °C hold for 75 minutes. The MS source operated with electron ionization (EI) and the temperature was kept at 230 °C. The temperature of the
quadrupole MS was kept at 150 °C. The chromatograms were acquired in the selective ion monitoring (SIM) mode.

The PAHs analysis was performed under the following temperature program: (1) 70 °C hold for 4 minutes, (2) temperature ramp from 70 °C to 300 °C at 10 °C min\(^{-1}\), (3) 300 °C hold for 31 minutes. The MS source operated with electron ionization (EI) and the temperature was kept at 230 °C. The temperature of the quadrupole MS was kept at 150 °C. The chromatograms were acquired in the selective ion monitoring (SIM) mode. The SIM program was designed to monitor the molecular \([M]^+\) and isotopic \([M+1]^+\) ions. It hasn’t been possible to resolve the isomer benzo[b]fluoranthene from benzo[j]fluoranthene (in the following notated as benzo[b+j]fluoranthene) and the isomer dibenzo[a,c]anthracene from dibenzo[a,h]anthracene (notated as dibenzo[a,c+a,h]anthracene).

Nitro-PAHs determination was carried out by gas chromatography-mass spectrometry (GC-MS) on a GC Agilent 6890N coupled with a MS PolarisQ ionic trap Thermo Fisher (Thermo Fisher Scientific Inc., Waltham, MA, USA) (Feilberg et al., 2001; Bamford and Baker, 2003). The separation was performed on an Agilent DB-5-MS fused silica capillary column (length 60 m, i.d. 250 μm, film thickness 0.25 μm). The injector was kept at 250 °C and 5 μL of sample were injected in pulsed splitless mode. Helium was used as carrier gas with a constant flow of 1.2 ml min\(^{-1}\). The nitro-PAHs analysis was performed under the following temperature program: (1) 70 °C hold for 1 minute, (2) temperature ramp from 70 °C to 300 °C at 10 °C min\(^{-1}\), (3) 300 °C hold for 25 minutes.

The ionic trap operated in negative chemical mode, with methane as reagent gas. The chromatograms were acquired in the selective ion monitoring (SIM) mode. The SIM program was designed to monitor the molecular \([M]^+\) and isotopic \([M+1]^+\) ions. Fragmentation voltages were selected by analysing standards at increasing fragmentation voltages. The voltages that gave the highest abundance of fragment ions were chosen for quantitation.

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

2.3 Quality assurance

The detection limits (LODs) of analytes, calculated as 3 times the average noise level (Feilberg et 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.
In order to quantify procedural recoveries, known volumes of surrogate standard solutions were added to samples prior to extraction. The recoveries of the spiked solutions were 79 ± 20 % for n-alkanes, 92 ± 27 % for PAHs and 105 ± 30 % for nitro-PAHs, by using 5α-androstane, benzo[a]pyrene-d12 and 4-nitro-para-terphenyl (Sigma Aldrich, Steinheim, Germany), respectively, as surrogates. Since satisfying recoveries were obtained, analyte concentrations in samples were not surrogate-corrected.

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

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

2.4 Meteorological conditions

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

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

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

3. Results

In previous works (Rossi et al., 2012; Sarti et al., 2015), the concentrations of particulate matter (PM_{1} and PM_{2.5}) and their seasonal and spatial variations in the sampling sites of the domain have
been reported. Some relevant results are herein briefly recalled: the PM$_{2.5}$ amount is higher in winter than in summer (averaged values of 33.7 ± 1.9 μg m$^{-3}$ and 19.68 ± 0.78 μg m$^{-3}$ respectively) and the PM$_1$ fraction accounts for the 79% in summer and for the 66% in winter of PM$_{2.5}$. In the following the n-alkanes, PAHs and nitro-PAHs composition of PM$_{2.5}$ and PM$_1$ is discussed. The average concentrations and the standard deviations of the analytes herein investigated are reported in Supplementary Information (Tables S2, S3 and S4).

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

### 3.1 n-alkanes

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 PM$_1$ and they constitute the 0.31% and 0.32% of PM$_{2.5}$ and PM$_1$ respectively. In winter, these 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 calculated on the basis of the values averaged on all the sampling sites (PM$_{2.5}$: MXW-2.5, CAS, CTS, CTW-2.5, MGA, MND, MXD-2.5 and MXS; PM$_1$: MXW-1, CTW-1 and MXD-1). These quantitative results indicate a larger concentration of alkanes in PM$_{2.5}$ in the cold season. Higher concentrations of alkanes in PM$_{2.5}$ collected in winter with respect to that sampled in summer were also observed in Thessaloniki (Chrysikou and Samara, 2009), in Milan (Perrone et al., 2012) and in Rome (Cecinato et al., 1999). This finding can be related to the increase in source emission from combustion and to stable meteorological conditions in the cold season which are unfavourable for the pollutants dispersion, as discussed in Paragraph 2.4.

**FIG 2**

The averaged concentrations of each n-alkane in PM$_{2.5}$ sampled in the sites of the domain during the summer and winter are reported in Figures 2a and 2b, respectively. Figure 2c and 2d show the mean concentrations of n-alkanes in the sampling sites during the two campaigns. It can be noted that, in MXD in summer (Fig. 2c) and in MXW in winter (Fig. 2d), the total concentration of n-alkanes in PM$_1$ is slightly higher than that in PM$_{2.5}$. This finding indicates that the n-alkanes in the two samples are preferentially partitioned in PM$_1$, the small differences between PM$_1$ and PM$_{2.5}$ can arise from the measurement errors.

By comparing Figs. 2a and 2c, it can be seen that in summer there is a predominance of even terms among short-chains n-alkanes (<C25). In winter, the concentrations of long-chain alkanes are generally higher than short-chain ones (see Figs. 2b and 2d).
To investigate on the possible sources classification (i.e. anthropogenic or biogenic) of n-alkanes, the Carbon Preference Index (CPI), describing the abundance distributions of the odd/even terms, was calculated for all the sites in both seasons. In addition to the CPI calculated for all the analysed homologues ($\text{CPI}_{15-32}$), the Carbon Preference Index for biogenic/pyrogenic ($\text{CPI}_{25-32}$) and for petrogenic n-alkanes (named $\text{CPI}_{14-25}$) have been calculated as follows (Górka et al., 2014):

\[
\text{CPI}_{15-32} = \frac{\sum (C_{15} - C_{31})}{\sum (C_{16} - C_{32})} \tag{1}
\]

\[
\text{CPI}_{25-32} = \frac{\sum (C_{25} - C_{31})}{\sum (C_{24} - C_{32})} \tag{2}
\]

\[
\text{CPI}_{14-25} = \frac{\sum (C_{15} - C_{25})}{\sum (C_{14} - C_{24})} \tag{3}
\]

Anthropogenic emissions from fossil fuel combustion generate a random distribution of odd vs. even terms yielding CPI$_{15-32}$ values close to 1. On the other hand, hydrocarbons originated from terrestrial plant material show a predominance of odd-numbered terms showing CPI$_{15-32}$ values higher than 3 (Simoneit, 1989).

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

\[
\%\text{WNA} = \frac{\sum_n\left(C_n - \frac{C_{n+1} + C_{n-1}}{2}\right)}{\sum_m C_m} \cdot 100 \tag{4}
\]

where $n = 25, 27, 29, 31$ and $m = 14, \ldots, 32$.

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

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

**TABLE 1**

Regarding CPIs it can be observed that in summer (see Table 1a) they follow a trend $\text{CPI}_{25-32} > \text{CPI}_{15-32} > \text{CPI}_{14-25}$ for all the sites, whereas in winter (Table 1b) the differences in CPIs are less significant. For most of the sites of the domain, CPI$_{25-32}$ values slightly decrease in winter with
respect to summer. This finding indicates that, for long-chain alkanes, the contribution of biogenic sources is more relevant in the warm season than in the cold one. On the contrary, CPI_{15-32} and CPI_{14-25} generally increase in the cold season, with values below 3, indicating that n-alkanes <C25 were primarily originated from fuel combustion processes.

3.1.1 n-alkanes in summer

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

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

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

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

3.1.2 n-alkanes in winter

In winter, the highest content of alkanes was measured in the suburban, the rural and the urban sites, CAS, MND and MGA, respectively (see Fig. 2d). In particular, CAS and MND are characterized by
high concentrations of long-chain homologues (>C25). These compounds typically come from plant
wax or from biogenic fuel burnings (Li et al., 2010; Simoneit et al., 1991). The low values of CPI25,
32 of CAS and MND indicate that in these sites long-chain alkanes have mainly pyrogenic origin
rather than biogenic (Górka et al., 2014). CAS is characterized by high PM10 concentration coming
from wood heating of the semi-rural suburban area, as demonstrated by specific high resolution
information about different heating fuels (natural gas, LPG and wood) (Rossi et al., 2012). MND
station is located in a rural area with low density of population, but the sampler was placed under
the influence of a domestic biomass combustion source emission not recognized during the
monitoring planning. For this reason, MND was considered not representative of the averaged
environment characteristics of the area in which it is located. The high concentration of alkanes
detected during the cold season in MND could thus derive from its peculiar location.

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

The highest concentration of n-alkanes in PM2.5 was found in MXW with respect to all the other
sites (i.e. MXW, CTS, CTW, MXD, MXS) (see Fig. 2d). The CPIs in Table 2b show that alkanes in
PM2.5 collected at MXW derive from both natural and anthropic sources, and the second ones seems
to prevail. MXD, despite the choice of being representative of the most polluted area in the domain,
exhibits a low content of n-alkanes in PM2.5; this is not in contradiction to the choice of the location
of this sampling site, because it is well known that n-alkanes sources emissions are very different
either in composition and in quantity and, first of all, not only related to pollutant sources.

To investigate about the partition of n-alkanes on different fractions of atmospheric aerosol, the
concentrations were normalized by the amount of particulate in the stations where both PM2.5 and
PM1 fractions were sampled (i.e. MXW, CTW and MXD). In winter MXW-1 and, to a lesser extent,
MXD-1 showed higher alkanes normalized concentrations than their respective PM2.5 (i.e. MXW-
2.5 and MXD-2.5). This finding indicates that these compounds are preferentially associated to the
finest fraction of PM, according to literature data (Bi et al., 2005; Pietrogrande et al., 2010). Indeed,
the ΣC14-C32 in PM1 accounts for about 100%, 40% and 75% of that in PM2.5 in MXW, CTW and
MXD, respectively. Furthermore, all the CPI values of PM1 samples are generally less than or equal
to that of the respective PM2.5 samples (see MXW and CTW in Table 1b), further confirming the
increasing contribution of anthropogenic alkanes with decreasing of PM size (Alves et al., 2000; Aceves and Grlmalt, 1993).

### 3.2 PAHs

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

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

**FIG 3**

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

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

By considering that PM$_{1}$ constitutes a high percentage of PM$_{2.5}$ (see Paragraph 3), it can be deduced that PAHs mainly accumulated in PM$_{1}$ in both seasons. This is in agreement with studies conducted elsewhere (Bi et al., 2005, Allen et al., 1996, Alves et al., 2000) which report that PAHs are mainly...
associated (60–90%) with the fine aerosol fraction. This preferred partition could derive from the higher adsorption of PAHs on the finest particles surface, due to their higher total surface area and lower water content (lower polarity) with respect to coarser particles (Allen et al., 1996). In addition, the dominance of PAHs in the smallest fraction is consistent with combustion processes as a major source of these particles (Crimmins, 2006; Masiol et al., 2012).

In winter, the sum of the concentrations of the isomers benzo[b]fluoranthene and benzo[j]fluoranthene (i.e. BbjF) has the largest dispersion with highest median value, as shown in Fig. 3b. These PAHs were found to be ones of the most abundant also in Baltimora (US) during Supersite investigations (Crimmins, 2006). In particular, the isomer benzo[b]fluoranthene was indicated as one of the marker of diesel-powered vehicles by Harrison et al. (1996). In Fig. 3b it can be also observed that in the cold season, high-molecular weight PAHs are the most abundant class, indeed 5-rings compounds account for almost 50% and 5- to 6-rings compounds account for almost 70% of all PAHs. Such distribution profiles could indicate that the major emission sources in wintertime are wood combustion and traffic, in agreement with other studies carried out in Northern Italy (Perrone et al., 2012; Vassura et al., 2014). In the following (see Paragraph 3.4), spatial and season variations of PAHs are discussed.

3.3 Nitro-PAHs

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

Unlike PAHs whose higher levels were observed during winter, nitro-PAHs concentrations were generally higher during the summer. This has been observed also in the Los Angeles basin by Reisen and Arey (Reisen and Arey, 2005) and can indicate that the origin of these nitro-derivatives in summer is mainly due to secondary processes. Nitro-PAHs in PM$_{1}$ were about 30% (winter) and 36% (summer) of those found in PM$_{2.5}$. However, by considering only sites where both PM$_{1}$ and PM$_{2.5}$ were sampled (i.e. MXW, CTW and MXD), the above percentages seem to be significantly different. In fact, in winter 88% of nitro-PAHs are concentrated into the finest fraction, while in summer this percentage is reduced to only 18%. A similar trend in the partition of nitro-PAHs during the cold and hot season has been also observed by Albinet et al. (2008), who report about larger nitro-PAHs values in super micrometer (> 1.3 μm) aerosol fraction in summer than in winter. In that work, it was proposed that the difference of
chemical affinities of the organic compounds with the super micrometer fraction of the aerosol could be responsible for the differences of size distributions of the nitro-PAHs. Another possible explanation has been proposed by Cecinato et al. (1999). Following these authors, heterogeneous reactions leading to secondary nitro-PAHs preferentially occur on coarser particles, due to the presence therein of metal oxides or salts acting as catalysers of such reactions. Both hypotheses could explain the observed trend. Based on these observations, the origin of nitro-PAHs in PM cannot be precisely attributed so that secondary origin of nitro-derivatives cannot be excluded.

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

**FIG 4**

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

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

In winter, CTS and MXS are characterized by a high 9-nitrophenanthrene concentration possibly due to biomass or industrial combustion processes.
3.4 PAHs seasonal and spatial distribution

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

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

FIG 5

PC1 accounts for differences in the total amount of PAHs since its variables loadings are very similar from each other. The average normalized concentrations of PAHs are higher for CTS and MXD (having lower PC1 scores) and, in particular, PAHs amount in the finest fraction of MXD is higher than what measured in the coarser fraction, similarly to what observed for n-alkanes (see Paragraph 3.1). The high PAHs content and their preferential partition into PM\(_1\) suggest a relevant contribution of anthropic combustion sources impacting this site (Cecinato et al., 1999; Crimmins, 2006), thus confirming that MXD represents a maximum of the domain as determined by the preliminary simulation study. Scores of MND and MGA on PC1 indicate that these sites contain relative lower amount of PAHs: also in this case this finding well agrees with the simulation study of emissions in the domain.

On PC2, low-molecular weight PAHs (especially naphtalene) have negative loadings, while benzo[g,h,i]perylene and indeno[1,2,3-cd]pyrene have high positive loadings. PC2 well discriminates MXD and CTS. In detail, MXD is characterized by high concentrations of low-molecular weight PAHs, which could be emitted by heavy-duty diesel vehicles (Ravindra et al., 2008). This site is indeed near freeways and railroads, hence characterized by high traffic. The high positive score of CTS on PC2 indicates concentrations higher than the average of benzo[g,h,i]perylene and indeno[1,2,3-cd]pyrene, mainly due to vehicles emissions. The attribution of a specific source of vehicular emission (i.e. gasoline- or diesel- fuelled vehicles) is difficult, since some studies report that emissions profiles of gasoline and diesel exhausts are rather similar (Harrison et al., 1996; Crimmins, 2006), while other works (Omar et al., 2002; Rinehart et al., 2006) indicate that higher molecular weight PAHs are mainly related to gasoline-fuelled vehicles. The average composition of PM\(_1\) in MXW and CTW is slightly enriched in low molecular weight PAHs...
with respect to PM$_{2.5}$. No differences were observed for the winter maximum MXW-2.5 and its control CTW-2.5, while the summer maximum MXS and its control CTS belong to different clusters. In addition to higher total content of PAHs than the average, the PM sampled in CTS is strongly enriched in anthracene and, to a lesser extent, in benzo[k]fluoranthene (high positive loading on PC3). The INP/BghiP ratio (see Table S5), which is the highest among all sites, together with concentrations of benzo[k]fluoranthene higher than the average suggest that CTS is impacted by diesel-fuelled vehicles emissions (Harrison et al., 1996), in addition to gasoline-fuelled ones (see PAHs diagnostic ratios in Supplementary Information).

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

**FIG 6**

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

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

Pyrene and fluoranthene have been identified to have reasonably high levels in emissions from several sources such as wood combustion, oil burning, industrial emissions, gasoline and diesel-powered vehicles, incineration (Ravindra et al., 2008; Cincinelli et al., 2007; Harrison et al., 1996). However, in the coarser fraction collected in MXW (i.e. PM$_{2.5}$) the relative concentrations of pyrene and fluoranthene do not significantly differ from those of other sites.

The lowest total levels of PAHs were measured in MXS.

PCA analysis on winter campaign was then performed by including 5 further analytes (i.e. cyclopenta[cd]pyrene, dibenzo[a,c+a.h]anthracene, dibenzo[a,l]pyrene, dibenzo[a,e]fluoranthene
and dibenzo[a,e]pyrene) to the above-mentioned 13. This wasn’t carried out in summer because concentration data of these additional PAHs were below the LOD in most cases. In fact, in summer concentrations lower of one order of magnitude than in winter were measured (see Fig. 3).

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

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

4. Conclusions

In this study the concentrations of n-alkanes in the range C14-C32, PAHs and nitro-PAHs were measured in PM$_{2.5}$ and PM$_1$ collected at 8 sampling sites around a municipal waste incinerator located near Bologna, in Emilia Romagna region (Northern Italy). The analysis of PM composition over the studied domain has been accomplished to investigate the similarities and differences between the various monitoring stations. This is the first step to bring out any evidence of impact of the different and peculiar local pollutant sources, like, for example, an incinerator plant. It was not possible clearly identify the contribution of the emissions of the incinerator itself in the domain, by analysing the selected organic compounds in PM. Nonetheless, some interesting findings have been pointed out. In particular, the PAHs concentrations in PM are higher of one order of magnitude in winter than in summer. Similarly, n-alkanes showed higher concentrations in the cold season even if the difference with respect to summer is smaller than PAHs. On the contrary, nitro-PAHs concentration in PM increases in hot season.

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

The results also showed that PAHs accumulate on the finest fraction of aerosol, especially in winter, while in summer nitro-PAHs are preferentially partitioned on the PM$_{2.5}$.
The highest total nitro-PAHs content was detected in summer in MXW-2.5 and in MXS and its control CTS in winter. Principal Components Analysis was performed on PAHs concentrations normalized by the PM amount. In summer, concentrations higher than the average were found in MXD, especially in the finest fraction of aerosol (i.e. MXD-1). This finding suggests a strong contribution of anthropic combustion sources, especially vehicular traffic, as it was expected due the location of this station. No significant differences were observed between MXW-2.5 and its control CTW-2.5, while MXS and its control CTS belong to different clusters.

In winter, in MXW-1 samples, the concentrations of pyrene, fluoranthene and benzo[b+j]fluoranthene higher than the average could be ascribed both to waste incineration and to diesel-powered vehicles. PAHs and n-alkanes showed the highest concentrations in the same PM$_1$ samples and in particular MXD-1 in summer and MXW-1 in winter.

**Acknowledgements**

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**Appendix A. Supplementary data**

Supplementary data related to this article are included.
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FIGURE CAPTIONS

Figure 1: Monitoring stations locations

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

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

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

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

Figure 6: Score and loading plots of the first three PCs based on the selected PAHs, for the winter campaign (data normalized). For PAHs abbreviations, see Table S3 in Supplementary Information.
Table 1: $C_{\text{max}}$, CPI indexes and %WNA for n-alkanes a) in summer and b) in winter

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Figure 6
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**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
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