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Seasonal trends and spatial variations of PM_{10}-bounded polycyclic aromatic hydrocarbons in Veneto Region, Northeast Italy

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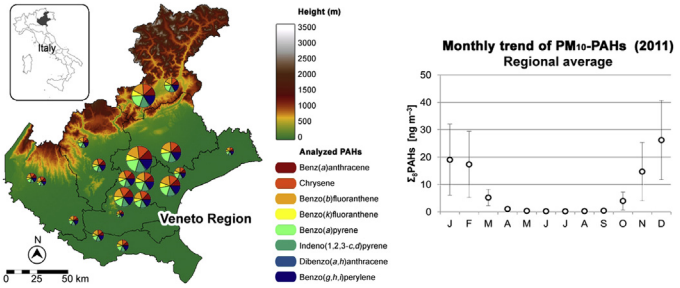
HIGHLIGHTS

- Eight PM_{10}-bound PAHs were monitored for 1 year in North-Eastern Italy.
- 21 stations of varying categories were selected: rural, urban, traffic, industrial.
- Seasonal trends and space distributions of PAH were discussed.
- PAHs were examined in relation to other air pollutants and weather conditions.
- Peculiar features of PAH pollution in the Region were characterized.

GRAPHICAL ABSTRACT



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ABSTRACT

The Veneto Region extends for $\sim 18.4 \cdot 10^3$ km^2 in the northeastern part of the Po Valley and includes mountains, hills, plain and coastal environments with very different and discontinuous anthropogenic pressures. Although many efforts have been made to mitigate air pollution, the European air quality standards for atmospheric pollutants are frequently breached. This study investigates the levels of eight PM_{10}-bound PAHs collected in 21 stations categorized as rural background, urban and suburban backgrounds, traffic and industrial hot-spots during one year (2011). Data were statistically processed to detect the PAH seasonal trends, their relationship with other air pollutants and micro-meteorological parameters and the space variations at a regional scale. Results show that PAHs levels are relatively high in the largest part of the region, with 10 sites exceeding the levels of BaP targeted by the European legislation. Two sites exhibited anomalously high PAHs concentrations and this anomaly became even more evident when considering the population density as a surrogate for the potential anthropogenic pressure. The PAHs levels were found directly proportional to other gaseous pollutants (CO, NO, NO_x, SO_2) suggesting common polluting sources. The analysis of time trends of PAH concentrations reveals significant coincidences throughout the region, i.e. simultaneous changes are observed in most sites as a consequence of similar emission sources and accumulation/removal processes. In this scenario, the control strategies currently imposed at local level (e.g. traffic limitations) have proven scarcely effective in mitigating air pollution and a real coordination at regional or even interregional level cannot be further postponed. Peculiar features of the PAHs pollution in the Veneto were also identified and some measures for protecting the human health were suggested.

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1. Introduction

The polycyclic aromatic hydrocarbons (PAHs) are mainly formed during the incomplete combustion and pyrolysis of organic material (Finlayson-Pitts and Pitts, 2000). PAHs are ubiquitously distributed in the troposphere due to natural combustions (e.g. volcanic activities, wildfires), although their presence in densely populated areas is largely due to anthropogenic processes including mobile sources, domestic heating, waste incineration, asphalt production, agricultural biomass burning, oil refining and many industrial activities (Boström et al., 2002; Marchand et al., 2004; Ravindra et al., 2008; Zhang and Tao, 2009). Being generally partitioned between the gaseous and particulate phases (e.g. Lammel et al., 2009), the 4-, 5- and 6-ring PAHs are predominantly particle-bound due to their high molecular weights and low volatilities. Despite their well documented toxic potential on humans and ecosystems (e.g. WHO, 2000; Billet et al., 2008; Andrysik et al., 2011; Tarantini et al., 2009; IARC, 2010), these compounds have been regulated only in few countries. In Europe, the Directive 2004/107/EC included the IARC class 1 human carcinogen benzo(*a*)pyrene (BaP) as indicator of particulate carcinogenic PAHs, by establishing an annual target value of 1 ng m^{-3} in PM_{10}. In addition, the Directive also requires that other relevant PAHs shall be monitored in a limited number of measurement sites.

The European emission inventories (EEA, 2012) indicate that Italy is one of the EU-27 member States most contributing (>10%) to the emissions of total PAHs in 2010 along with Belgium, Germany, Poland and Spain and the Italian emission inventories (ISPRA, 2012) reported that Veneto is among the five Regions most contributing to the atmospheric PAHs in Italy. This worrying scenario is largely confirmed by experimental data evidencing that the BaP European air quality target value is breached in many locations of Veneto (Rampazzo et al., 2008; ARPAV, 2010, 2011, 2012). Since BaP is reported frequently exceeding the target values in the largest cities (ARPAV, 2012) with the subsequent increasing risk for living people, the Veneto Region administration is urged to develop and implement control and mitigation strategies.

Nevertheless, the so far available data on PM_{10}-bound PAHs at regional scale remain incomplete and many questions still need to be addressed. This study was carried out to measure the levels of eight PM_{10}-bound PAHs collected in 21 sampling stations distributed all over the region and categorized as rural, urban and semi-urban backgrounds, traffic and industrial hot spots. Analyzed PAHs were chosen to be consistent with the European Directive and include the higher molecular weights congeners of the US-EPA priority pollutant list, i.e. those mainly partitioned in the particulate phase. The comprehensive dataset discussed in this study has been statistically investigated to detect the PAH seasonal trends, their relationship with other air pollutants and micro-meteorological parameters and their space variations at a regional scale. Results are discussed to identify the critical features of the PAHs pollution in the Veneto and help outlining some measures to protect the human health.

2. Study area

Veneto (Fig. 1a), one of the 20 administrative Regions of Italy, is located in its northeastern part and extends over $\sim 18.4 \cdot 10^3$ km^2, with a maximum extension of ~210 km on the North–South and ~195 km on the West–East axes. From a geomorphological point of view, it includes very different environments ranging from the northern Alpine zone (29% of the territory), to the intermediate hill zone (15%), the southern lower plain (56%) and the eastern coastland (Fig. 1b). The northern part is mainly occupied by mountains and hilly areas largely covered by grasslands and forests, where the scarce urbanization, population density and industrialization are mainly concentrated in the valleys. In contrast, to the South, Veneto extends over the eastern part of the Po Valley, where some large cities (Venice-Mestre, Padova, Vicenza and Verona) are spaced by a number of scattered urban settlements, industrial areas and agricultural/rural environments. In this area, the high anthropogenic pressure combined with peculiar weather conditions favor pollutant accumulation and nucleation events (e.g. Hamed et al., 2007; Squizzato et al., 2013), which are mainly responsible for the highest levels observed for many atmospheric pollutants (EEA, 2013).

In 2011 the Veneto population distributed in 7 Provinces and 581 Municipalities, which are very different in surface extension, geomorphology, population density and industrialization levels (Table 1) counted ~4.9 Million inhabitants: ~4 Million with an age above 20 years, ~879,000 from 1 to 19 years and ~94,000 below 1 year (ISTAT, 2012).

3. Materials and methods

3.1. Sites selection

In 2011 (January–December) a sampling campaign was carried out by ARPAV (Veneto Agency for Environmental control) in 21 sites of the Region to collect PM_{10} on daily filters for PAHs analyses. The sites were included in the Regional plan for the protection and renewal of the atmosphere (Veneto Region, 2013). The map of selected sites is reported in Fig. 1a and b, along with the Province boundaries and the terrain relief map, respectively. Table 1 summarizes some site characteristics. A total of 4 rural background sites (RUR) defined by the EU Directive 2008/50/EC have been selected: BL-RUR is located in an alpine pass at 2020 m a.s.l. and is representative of high mountain environments; PD-RUR, VE-RUR and RO-RUR are located in agricultural areas of the Po Valley not directly influenced by heavy traffic roads, urban or industrial settlements. Eight urban (URB) and two suburban (SUB) background sites were placed in high density residential areas. Being broadly representative of city-wide background levels of air pollutants, URB and SUB sites are thus very important for assessing the potential health hazard for living people. Three roadside sites were selected as automotive traffic hot-spots (TRA), being located near heavy traffic roads in the three most populated cities of the Region (Venice-Mestre, Padova, Verona). Finally, four sites in the PD province were chosen as representative of different industrial areas (IND): the station PD-IND1 is located in an area near Padova downwind to the emissions of a steelworks; PD-IND2 and PD-IND3 are placed in an urbanized area of Padova close to a large municipal solid waste incinerator (MSWI); PD-IND4 is sited in the town of Monselice near a cement plant.

3.2. Samplings and analytical procedures

Samplings were carried out according to EN 12341:1998 standard on quartz fiber filters (Whatman QMA, GE Healthcare, USA) and were continuous for 24 h starting at midnight. PM_{10} masses were measured automatically, using beta radiation attenuation monitors (BAMs), or manually, following the standard gravimetric determination with a micro-balance (sensibility 0.1 μg) at constant temperature (20 ± 1 °C) and relative humidity (50 ± 5%). Careful validations studies were conducted between the gravimetric and BAMs methods before the sampling campaign. In addition, several tests were also routinely performed (at least 1 test every week) to constantly check the BAMs. The validations include pairs of filters measured with both methods and the results were then verified to be within the variation margins imposed by the technical regulations in force

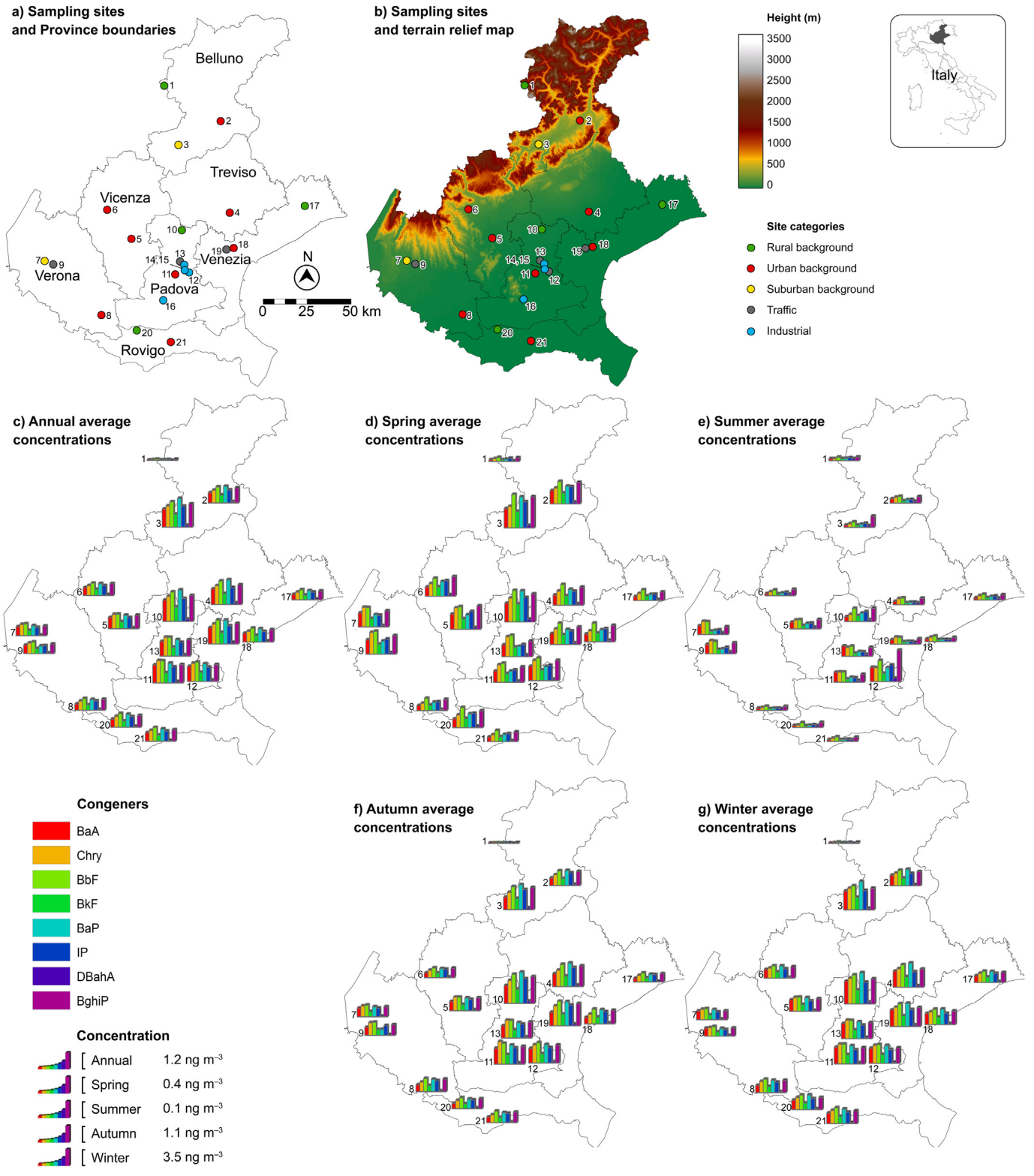

Fig. 1. Map of selected sampling sites showing also the boundaries of the Provinces, (a) the terrain relief (b), the annual (c) and seasonal (d–g) average concentrations measured for all analyzed congeners and sites.

UNI EN 12341:2001. Generally, good agreement between the two methods was found. The list of used methods for each site is available in Supplementary material Table 1. Sampled filters were stored in clean Petri slides in the dark and at −20 °C until extraction to avoid PAH degradation and losses.

Eight PM_{10}-bound PAHs including benz(*a*)anthracene (BaA), chrysene (Chry), benzo(*b*)fluoranthene (BbF), benzo(*k*)fluoranthene (BkF), BaP, indeno(1,2,3-*c*,*d*)pyrene (IP), dibenzo(*a*,*h*)anthracene (DBahA) and benzo(*g*,*h*,*i*)perylene (BghiP) were identified and quantified after solvent extraction. A 2695 series Alliance

Table 1
Characteristics of the selected sampling sites and number of analyzed samples.

N	Province	Municipality (location)	Site acronym and categorization[a]	Lat.–Long.	Height (*m*)	Site characteristics[b]	Nr of analyzed samples
1	BL	Falcade (Passo Valles)	BL-RUR	46.339 N–11.802 E	2020	Alpine pass distant from direct sources	190
2	BL	Belluno	BL-URB	46.143 N–12.218 E	401	Public park in the city center (37,000)	190
3	BL	Feltre	BL-SUB	46.030 N–11.905 E	263	Residential area (21,000)	201
4	TV	Treviso	TV-URB	45.672 N–12.238 E	15	City center (84,000)	127
5	VI	Vicenza	VI-URB	45.560 N–11.539 E	36	City center (116,000)	175
6	VI	Schio	VI-URB2	45.714 N–11.368 E	190	City center (40,000)	181
7	VR	Legnago	VR-URB	45.183 N–11.311 E	25	City centre (25,000)	161
8	VR	Verona (Cason)	VR-SUB	45.462 N–10.911 E	91	Agricultural area distant from direct sources (270,000)	169
9	VR	Verona	VR-TRA	45.444 N–10.963 E	62	City centre, near a major road (264,000)	109
10	PD	S. Giustina in Colle	PD-RUR	45.594 N–11.909 E	24	Agricultural area away from direct sources (7000)	178
11	PD	Padova (Mandria)	PD-URB	45.371 N–11.841 E	13	Residential area (215,000)	160
12	PD	Padova (Arcella)	PD-TRA	45.433 N–11.890 E	11	Major road in residential/commercial area of Padova (215,000)	180
13	PD	Padova (Granze)	PD-IND1	45.378 N–11.940 E	8	Residential area of Padova (215,000) near a steel mill	176
14	PD	Padova (2)	PD-IND2	45.415 N–11.907 E	10	Residential area of Padova (215,000) near a MSWI	179
15	PD	Padova (1)	PD-IND3	45.395 N–11.909 E	10	Residential area of Padova (215,000) near a MSWI	152
16	PD	Monselice	PD-IND4	45.244 N–11.750 E	14	Residential area (18,000) near a cement plant	132
17	VE	Concordia Sagittaria	VE-RUR	45.694 N–12.786 E	5	Agricultural area away from direct sources (11,000)	125
18	VE	Venice (Mestre Bissuola)	VE-URB	45.498 N–12.261 E	1	Public park in the city centre of Mestre (271,000)	157
19	VE	Venice (Mestre v. Tagliamento)	VE-TRA	45.490 N–12.218 E	4	Mestre residential area (271,000) near expressway and major roads	182
20	RO	Badia Polesine	RO-RUR	45.103 N–11.554 E	8	Agricultural area away from direct sources (11,000)	178
21	RO	Rovigo	RO-URB	45.039 N–11.790 E	3	City centre (53,000)	175

[a] Categorization defined by EEA (1999); RUR = rural background; URB = urban background; SUB = suburban background; TRA = traffic hotspot; IND = industrial.
[b] The population number is provided within brackets and refers to the entire Municipality. MSWI: municipal solid waste incineration plant.

HPLC (Waters, USA) with quaternary pump, auto-sampler, micro-degasser, column thermostat and interfaced with a 2475 multi λ fluorescence detector was used. From 1 to 3 filters were ultrasonically extracted together for 15 min in 5–15 mL of acetonitrile (HPLC grade, ≥99.9%, Sigma–Aldrich, USA) and the extracts were then filtered on PTFE syringe filters (porosity 0.2 μm). HPLC set-up was the following: reversed phase chromatographic column (LC-PAH, 15 cm × 3 mm, 5 μm, Supelco, USA) at a temperature of 25 °C, injection volume 5 μL, mobile phase system consisting in a ramp mixture of ultrapure H_2O and acetonitrile at a flow rate of 0.5 mL min^{-1}. Some additional information about the adopted analytical methods are provided as Supplementary material Table 2.

3.3. QA/QC

Five diluted aliquots of a standard containing the EPA's 16 PAHs (Ultra Scientific, USA) were used to calibrate the instrumental response. The analytical method was validated by systematically measuring the certified reference material ERM CZ100 PAHs (JRC, Belgium): recovery efficiencies ranged between 75% and 125%. The limit of detections (LODs) were calculated measuring surrogate standards with 0.5 ng mL^{-1}. Considering the average air volume sampled, the calculated LODs were 0.02 ng m^{-3} for all the congeners. Blank filters were prepared and analyzed together with the samples, verifying that PAHs values were under the LODs.

3.4. Micro-meteorological parameters and automatic measure of atmospheric pollutants

In a number of sites the micro-meteorological parameters were systematically recorded with automatic instruments: air temperature (°C), solar radiation (W m^{-2}), relative humidity (%), atmospheric pressure (mbar), precipitation (mm) and the average speeds of the prevailing winds (m s^{-1}). The following chemical parameters were also automatically determined: $PM_{2.5}$ with BAMs, CO following the EN 14626 standard method based on non-dispersive infrared spectroscopy, NO, NO_2, NO_x according to EN 14211 standard method based on chemiluminescence, SO_2 with the fluorescence method EN 14212 and O_3 using ultraviolet photometry described in EN 14625 standard. A comprehensive list of measured parameters in each site is provided in Supplementary material Table 1.

3.5. Toxic and mutagenic equivalency factors

BaP was historically considered the most carcinogenic PAH and is often used as an indicator of human exposure to PAHs. However, virtually all congeners are recognized having potential carcinogenic effect and the toxic equivalency factor (TEF) method has been largely used to assess the carcinogenic potential of PAHs mixtures (Boström et al., 2002). BaP-like toxic equivalents (BaP_{TEQ}) are then calculated as:

$$BaP_{TEQ} = \sum(PAH_i \times TEF_i)$$

where PAH_i and TEF_i are the concentration and TEF for the *i* congener. TEFs from Nisbet and LaGoy (1992) were used as the most reliable indexes for studies on the toxicity of PAHs in atmospheric particulate matter and to be consistent with similar recent studies (e.g., Silva et al., 2010; Han et al., 2011; Delgado-Saborit et al., 2011; Masiol et al., 2012a; Cristale et al., 2012; Zhou and Zhao, 2012). Similarly, just with the replacement of TEF with MEF (Mutagenic Equivalency Factors) proposed by Durant et al. (1996), the mutagenicity related to BaP (BaP_{MEQ}) was also calculated.

4. Results

4.1. Overview on PM_{10} levels

In 2011, PM_{10} concentrations in ten sampling stations exceeded the annual average concentration (AAC) limit fixed by the 2008/50/EC Directive: 40 μg m^{-3} averaged over a calendar year (Table 2). In five sites the values were equal to or below this limit, but in all cases above the target values of 20 μg m^{-3}. In the alpine site BL-RUR the lowest AACs were found: 7 μg m^{-3}. Unfortunately, the PM_{10} AAC in

Table 2
Statistics for PM_{10} and Σ_8PAHs levels on seasonal and annual basis. All values are expressed in μg m^{-3} and ng m^{-3}, respectively.

Site	PM_{10}	Σ_8PAHs									
	Annual	Spring		Summer		Autumn		Winter		Annual	
	Mean (no. of daily excedances)[a]	Mean	Min–Max	Mean	Min–Max	Mean	Min–Max	Mean	Min–Max	Mean	Min–Max
BL-RUR	7 (0)	0.4	0.1–1.4	0.1	0.1–0.2	0.2	0.1–1.3	1.2	0.3–3.9	0.5	0.1–3.9
BL-URB	23 (19)	2.6	0.3–8.6	0.2	0.1–0.3	5.9	0.1–25.6	20	7.8–45.1	7.1	0.1–45.1
BL-SUB	28 (56)	3.9	0.2–14.8	0.2	0.1–0.5	9.5	0.1–33.5	33	12.2–58.8	11.8	0.1–58.8
TV-URB	43 (102)	2.2	0.2–10.2	0.2	0.1–0.3	9.1	0.2–38.6	27.9	10–78.6	10	0.1–78.6
VI-URB	46 (112)	2.7	0.3–14.1	0.3	0.2–0.5	5.7	0.4–20.1	18.6	7.9–28.5	6.6	0.2–28.5
VI-URB2	29 (41)	2.2	0.2–8.7	0.2	0.1–0.2	3.9	0.1–13.4	15.8	8.1–34.5	5.4	0.1–34.5
VR-URB	n.m.	1.3	0.2–7.3	0.1	0.1–0.2	5.2	0.1–22.8	16.4	3.5–35.1	4.9	0.1–35.1
VR-SUB	35 (68)	2.2	0.3–8	0.3	0.2–0.6	4.7	0.2–20.9	13.8	6.6–20.9	5.1	0.2–20.9
VR-TRA	48 (129)	2.5	0.3–8	0.3	0.2–0.6	4.8	0.3–11.2	11.9	4.6–18.5	4.7	0.2–18.5
PD-RUR	43 (99)	3.8	0.3–12.1	0.3	0.1–0.8	12	0.2–66.1	37.8	11.5–70	13.1	0.1–70
PD-URB	44 (93)	2.1	0.2–7.4	0.3	0.2–0.6	8.8	0.6–35.9	25.4	9.7–46.9	9.7	0.2–46.9
PD-TRA	42 (95)	2.2	0.2–9	0.3	0.2–0.5	7.2	0.4–32.2	23.9	7.5–47.2	8.3	0.2–47.2
PD-IND1	45 (102)	2.6	0.2–8.1	0.7	0.2–3.5	8.3	0.4–36.4	24.2	9.8–44.8	8.5	0.2–44.8
PD-IND2	39 (93)	2.2	0.1–7	0.2	0.1–0.3	6.6	0.2–27.9	23.5	8–45.5	7.9	0.1–45.5
PD-IND3	46 (100)	3	0.1–9.6	0.3	0.1–1.4	9	0.3–22.9	23.9	9.1–42.7	9.4	0.1–42.7
PD-IND4	n.m.	1.9	0.2–8.4	0.2	0.1–0.5	4	0.4–18.1	12.7	5.4–27.6	3.8	0.1–27.6
VE-RUR	35 (55)	1	0.1–5.3	0.2	0.1–0.4	3.4	0.2–11.8	14	2.8–31.2	4.2	0.1–31.2
VE-URB	39 (91)	1.9	0.2–8.8	0.1	0.1–0.2	5.6	0.1–31.5	19.1	5.8–43.5	5.9	0.1–43.5
VE-TRA	46 (108)	2.3	0.3–8.2	0.2	0.1–0.3	9.8	0.2–39.5	28.6	8.2–55.3	10.3	0.1–55.3
RO-RUR	40 (94)	1.9	0.2–7	0.1	0.1–0.2	4.2	0.1–18	16.7	4.8–42.2	5.7	0.1–42.2
RO-URB	41 (90)	1.2	0.1–4.4	0.1	0.1–0.2	4.3	0.1–14.6	17.2	3.8–34.6	5.9	0.1–34.6
Veneto		2.2 ± 2.8	0.1–14.8	0.2±0.3	0.1–3.5	6.3 ± 8.7	0.1–66.1	20.8 ± 13.7	0.3–78.6	7.2 ± 11.4	0.1–78.6

[a] Number of days exceeding the 24-h concentration of 50 μg m^{-3}; n.m. = not measurable.

VR-URB was not measured, whereas in PD-IND4 it could not be computed for the whole year due to a failure of the beta attenuation monitor in winter. The European Directive also states that the 24-h limit value of 50 μg m^{-3} must not be exceeded more than 35 times in a calendar year. Experimental results revealed that this limit was met in only two sites (BL-RUR and BL-URB). The 24-h limit was frequently exceeded in the remaining sites (Table 2), with the highest number (>100) of exceeding days in the largest cities (Venice-Mestre, Padova, Verona, Vicenza and Treviso).

4.2. PAHs levels

A total of 3477 samples were analyzed for PAHs. Table 1 lists the number of analyzed samples for each site, whereas Table 2 summarizes some statistics on seasonal and annual basis. For this purpose concentrations below the LODs were substituted by LOD/2. A comparison of the PM_{10} levels measured in all samples of 2011 with those determined in the samples analyzed also for PAHs does not show significant differences. This fact allows to extend the results of the study to the whole year. The map of the annual average values measured for all congeners in each site is drawn in Fig. 1c. The annual mean (3477 samples) of the sum of the analyzed congeners (Σ_8PAHs) was 7.2 ng m^{-3}. The maximum value of Σ_8PAHs (78.6 ng m^{-3}) was recorded in TV-URB in January. However a series of samples with high concentrations (up to 70 ng m^{-3}) was found in PD-RUR, which is categorized as a rural background. Generally the lowest concentrations were found in the high mountain site of BL-RUR, with values frequently below the LODs. The mean PAH profiles (percent contribution of each congener to Σ_8PAHs) for each site are provided as Supplementary material Fig. 1. No significant differences in the PAHs profiles were found and, on average, the most abundant congener was BbF (18%), followed by BaP (17%), BghiP (15%), Chry (15%), IP (13%), BaA (12%), BkF (8%) and DBahA (1%).

The annual regional average concentrations of the class 1-carcinogen BaP (average of all 3477 samples) was 1.2 ng m^{-3}, i.e. slightly above the target value of 1 ng m^{-3} imposed by the European Directive. As for Σ_8PAHs, the maximum value of BaP (13.5 ng m^{-3}) was recorded in TV-URB on January, whereas a series of days with very high concentrations (>12 ng m^{-3}) was found in the rural site of PD-RUR. The lowest concentrations were found in BL-RUR. The results show that a total of 10 sites exceeded the EU limits, whereas the limit was equaled, but not exceeded, in 4 sites. Comparing these results with those of similar studies (Supplementary material Table 3), the annual concentrations of BaP were among the highest recorded in Europe. In particular, BaP values were relatively similar to those of many other EU cities in spring, summer and autumn, whereas they appear to be among the highest in winter.

5. Discussion

All stations were assigned to different categories on the basis of their location and data previously obtained. It was expected that in rural sites PAHs concentrations should be lower than in urban background, traffic or industrial ones. However experimental results revealed that this assumption proved to be true in the Provinces of BL, VE and RO, but not in PD, where in the rural site PD-RUR PAHs concentrations were higher than in PD-URB, PD-TRA and PD-INDs supposed more anthropized. This result, although unexpected on the basis of the station classification was in agreement with previous data recorded in the station (ARPAV, 2011, 2012). The PAH values in the VI and VR Provinces, for which no rural background sites were available, indicate that the PAH levels are lower than PD-RUR, which is the closer rural site, but higher than other rural sites located in the Po Valley (VE-RUR and RO-RUR). PD-RUR is located in a rural area, not directly influenced by large agglomerations and very far from direct anthropogenic sources such as traffic roads or industrial installations. However, the site is geographically located in the middle of the most anthropized part of Veneto (in the middle of four major cities: Mestre-Venice, Treviso, Vicenza and Padova) and for this reason it should be probably classified differently. In

any case, an unknown local source of PAH, such as a large use of wood combustion for domestic heating, may be also present and should be investigated in further studies.

5.1. Seasonal variations

The regional average concentration of PM_{10} exhibited a pronounced seasonal trend with higher levels during the cold seasons and lower in summer in general agreement with all Northern Italy. In the cold season conditions of atmospheric stability and reduced mixing of lower layers favor the accumulation of atmospheric pollutants close to the ground (Pecorari et al., 2013). Moreover, the increased use of wood for domestic heating in cold seasons and the bulk burning of biomasses like straw and crop residues in the harvest season may also be responsible of high PM_{10} levels in late autumn and winter. This assumption is largely confirmed by the increasingly use of wood and softwood (i.e. logs, briquettes, chips and pellet) in northern Italy (Pastorello et al., 2011), whereas there is no evidence in the use of charcoal as household fuel. BL-RUR has an opposite behavior with higher values in the warm season. This result could be due to the peculiar characteristics of the site, in a high-mountain remote location, where the effects of anthropogenic local emissions are negligible and long-distance transport may be remarkable. For most of the year the area is completely covered with snow, whereas during few summer months dust can be released from both igneous rocks and sandstone by wind deflation. During the warm period, the site is probably within the planetary boundary layer (PBL) and therefore it reflects the effect of PM_{10} resuspension from the valley ground. In all cases, it is assumed that the local resuspension of crustal dust may play an important role.

The maps of the average PAHs concentrations measured for each congener and site on a seasonal basis are shown in Fig. 1d–g, whereas the seasonal concentrations of Σ_8PAHs for each site are reported in Fig. 2a. The PAHs mass ratio (Σ_8PAHs/PM_{10}, in ng μg^{-1}) can be used as an indicator of variability in PAH levels relative to PM_{10} masses and in this study it was computed only for days for which both PM_{10} and PAHs concentrations above the LODs were available. The results are shown in Fig. 2b. Significant seasonal variations have been recorded in all sites, with generally higher levels of Σ_8PAHs in winter (regional average concentration of 21 ng m^{-3}), followed by autumn (6.3 ng m^{-3}), spring (2.2 ng m^{-3}) and summer (0.2 ng m^{-3}). The monthly variations are provided as Supplementary material Fig. 2 and show that the most significant changes in Σ_8PAHs occur simultaneously in all the sites between February and April (strong decrease) and in October and November (fast increase). These periods coincide with the most significant changes in the air temperature, but are also consistent with the periods in which domestic heating is switched off (15 April) and on (15 October) according to the national legislation.

It is interesting to point out that the seasonal trend of PAHs was in phase with that of PM_{10}, with higher values in the cold autumn and winter, but it was somehow "amplified": the variations of PAH mass ratios are more pronounced than those of PM_{10}. This fact can be explained by a combination of several factors. These include the aforementioned weather conditions driving the pollutant accumulation in atmosphere during the cold season, but also the atmospheric photochemistry. PAHs concentrations can be affected by photo- and chemical oxidations triggered by the solar radiation and carried out by a number of atmospheric oxidants such as ozone and radicals (hydroxyl, NO and NO_2) (Arey and Atkinson, 2003; Esteve et al., 2004, 2006; Ringuet et al., 2012), which decompose PAHs during the warmest seasons. Moreover, wintertime levels can be also enhanced because of the increasing sorption of the most volatile PAHs on particles because of the decreased air temperature (Ravindra et al., 2006; Galarneau, 2008).

The relationships of Σ_8PAHs with other air pollutants and micro-meteorological factors were also investigated in more detail. Before any statistical analysis, all the variables were tested for normality by applying the Shapiro–Wilk tests. As the normality assumption at $p < 0.05$ was not met, the intra-variable relationships were computed using the Spearman's correlation analysis, which is performed on ranked data and outputs ρ values. The correlations of Σ_8PAHs with the micro-meteorological parameters and air pollutants in sites differently categorized and spatially located are reported in Table 3. Significant ($p < 0.01$) negative correlations were found with ozone, air temperature, solar radiation and average speeds of prevalent winds, confirming the important role of the former parameters in the oxidation processes. However, this also shows that the local atmospheric circulation in the whole study area significantly affects the PAHs levels. As evidenced in a recent study conducted in Venice-Mestre (Masiol et al., 2012b), fast winds

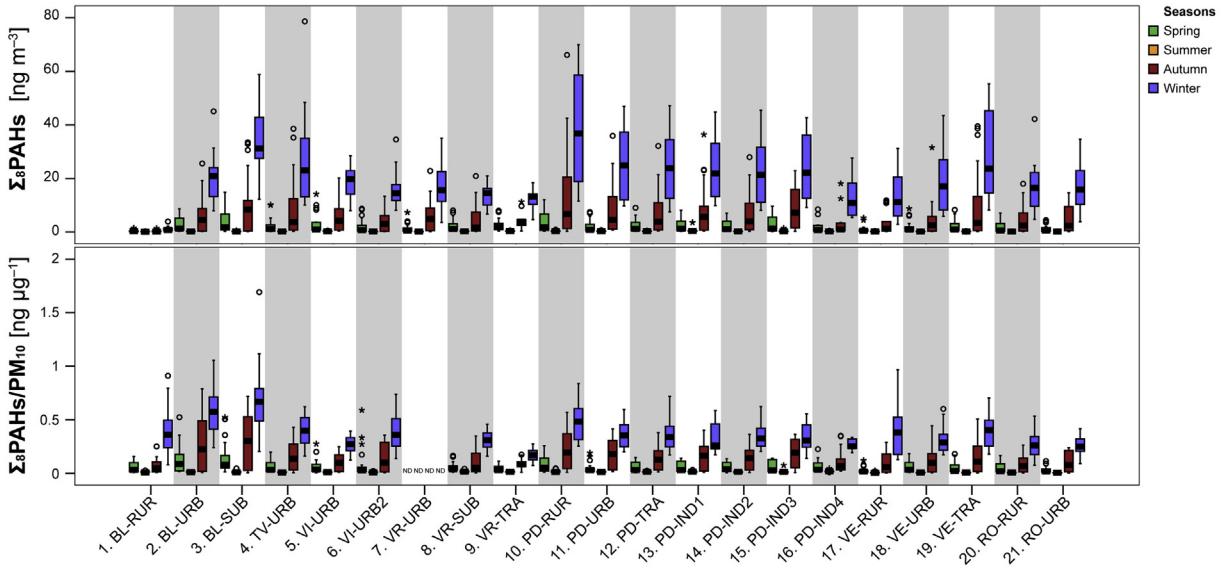

Fig. 2. Seasonal values of the sum of the analyzed congeners (Σ_8PAHs) and PAHs mass ratio (Σ_8PAHs/PM_{10}) for all sites.

Table 3
Spearman's correlations (ρ) of Σ_8PAHs with the micro-meteorological parameters and air pollutants calculated in different sites. Significant correlations at $p < 0.01$ are marked in bold font.

	Annual					Spring			
	BL-SUB	VR-SUB	PD-URB	PD-TRA	PD-IND2	BL-SUB	VR-SUB	PD-URB	PD-TRA
PM_{10}	**0.74**	**0.70**	**0.87**	**0.83**	**0.87**	**0.63**	**0.61**	**0.72**	**0.72**
$PM_{2.5}$	–	**0.77**	–	–	**0.90**	–	**0.81**	–	–
$PM_{2.5-10}$	–	−0.15	–	–	0.23	–	−0.50	–	–
CO	**0.96**	**0.80**	**0.92**	**0.97**	**0.94**	**0.88**	0.39	**0.79**	**0.95**
NO	**0.91**	**0.82**	**0.90**	**0.96**	**0.93**	0.32	**0.64**	0.65	**0.86**
NO_2	**0.91**	**0.83**	**0.81**	**0.82**	**0.88**	**0.95**	0.59	0.54	**0.85**
NO_x	**0.94**	**0.88**	**0.93**	**0.96**	**0.94**	**0.94**	**0.69**	0.59	**0.90**
SO_2	−0.09	**0.65**	**0.75**	0.23	0.21	−0.38	0.59	0.63	−0.26
O_3	**−0.86**	**−0.87**	**−0.61**	**−0.88**	**−0.92**	**−0.66**	**−0.83**	**−0.83**	**−0.90**
Air temperature	**−0.96**	**−0.93**	**−0.90**	**−0.93**	–	**−0.89**	**−0.80**	**−0.89**	**−0.89**
Solar radiation	–	**−0.82**	**−0.82**	**−0.73**	–	–	**−0.72**	**−0.91**	**−0.78**
Relative humidity	**0.49**	**0.38**	**0.73**	**0.61**	–	0.32	0.14	**0.85**	**0.66**
Atmospheric pressure	**0.36**	**0.46**	**0.50**	–	–	0.22	0.57	0.30	–
Average prevailing wind speed	**−0.55**	**−0.48**	**−0.56**	**−0.63**	−0.31	−0.46	−0.22	0.14	0.12
Rain	–	−0.13	−0.19	−0.18	–	–	0.15	0.52	0.43
	Autumn					Winter			
	BL-SUB	VR-SUB	PD-URB	PD-TRA	PD-IND3	BL-SUB	VR-SUB	PD-URB	PD-TRA
PM_{10}	0.68	**0.55**	**0.66**	**0.73**	**0.83**	**0.55**	**0.50**	**0.79**	**0.70**
$PM_{2.5}$	–	0.54	–	–	**0.88**	–	0.48	–	–
$PM_{2.5-10}$	–	−0.52	–	–	0.02	–	0.16	–	–
CO	**0.96**	**0.74**	**0.84**	**0.97**	**0.91**	**0.89**	**0.86**	**0.92**	**0.89**
NO	**0.91**	**0.89**	**0.88**	**0.95**	**0.92**	**0.79**	0.51	**0.80**	**0.88**
NO_2	**0.91**	0.56	0.17	0.22	**0.80**	**0.61**	0.35	0.51	**0.80**
NO_x	**0.95**	**0.82**	**0.82**	**0.89**	**0.92**	**0.83**	0.50	**0.81**	**0.89**
SO_2	0.22	**0.68**	**0.69**	**0.53**	0.06	0.37	−0.07	0.51	0.28
O_3	**−0.96**	**−0.96**	−0.52	**−0.94**	**−0.96**	**−0.66**	−0.33	0.56	−0.01
Air temperature	**−0.96**	**−0.97**	**−0.91**	**−0.98**	–	**−0.51**	**−0.64**	−0.48	−0.44
Solar radiation	–	**−0.83**	**−0.65**	–	–	–	−0.19	0.09	−0.03
Relative humidity	0.38	**0.59**	0.63	**0.50**	–	0.20	−0.01	0.01	−0.15
Atmospheric pressure	**0.61**	0.61	**0.70**	–	–	0.40	0.57	0.26	–
Average prevailing wind speed	−0.41	**−0.55**	−0.42	−0.43	−0.52	−0.41	−0.17	**−0.73**	**−0.69**
Rain	–	0.04	−0.33	−0.37	–	–	−0.11	−0.25	−0.20

may move large air masses and cause lower levels of particle-phase PAHs, whereas in presence of scarce ventilation, locally emitted PAHs are trapped and concentrations increase. On the contrary, significantly positive correlations were found in all the sites with most of the air pollutants (PM_{10}, $PM_{2.5}$, CO, NO, NO_2, NO_x, SO_2), relative humidity and atmospheric pressure. This result shows that most of the monitored pollutants are strongly linked to one another and suggests that the same emission sources act for the formation of these pollutants, while similar atmospheric processes are responsible for their variations. In particular, the correlations between PAHs and $PM_{2.5}$ appear greater than those with PM_{10}, confirming that PAHs are mainly absorbed onto finer particles, whereas

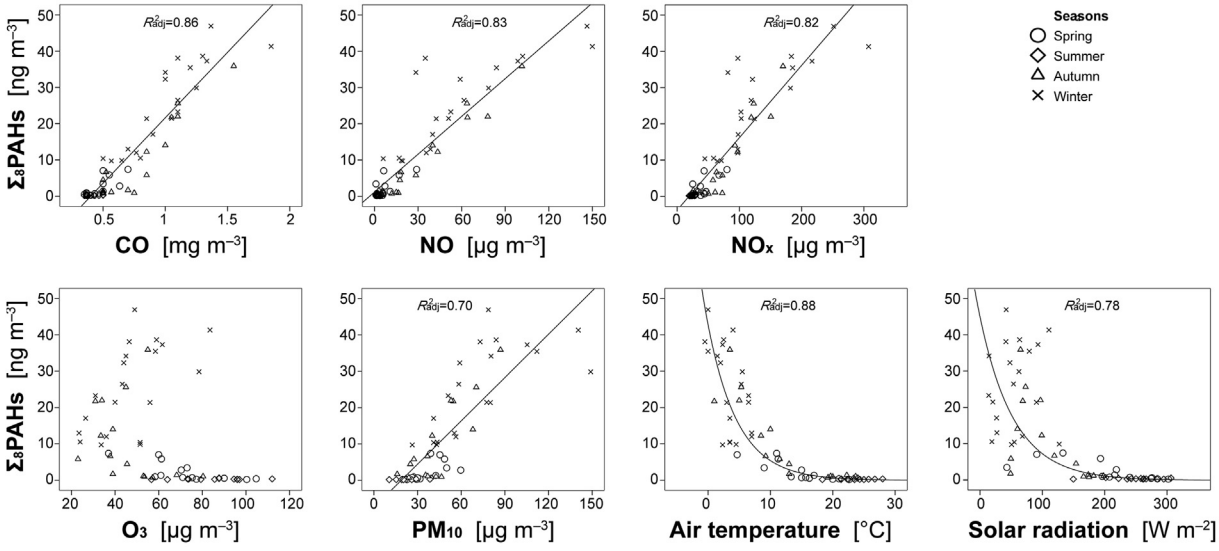

Fig. 3. Scatterplots of Σ8PAHs versus atmospheric pollutants and micro-meteorological parameters recorded in the Padova urban background site (PD-URB) in spring (circles), summer (diamonds), autumn (triangles) and winter (crosses). Interpolating functions were also plotted when significant (Determination coefficient > 0.6.

no correlations were found between Σ_8PAHs and coarse particulate matter ($PM_{2.5-10}$).

Although PAHs are strongly linked to some micro-meteorological parameters and air pollutants, these relationships are not necessarily linear. To render more evident the relationships resulting from the correlation analyses, the scatterplots of Σ_8PAHs versus measured atmospheric pollutants and micro-meteorological parameters recorded in the urban background site of a major city (PD-URB) are shown in Fig. 3. The plots suggest that the PAHs levels are linearly dependant on CO, NO, NO_2, NO_x, SO_2 and PM_{10}. On the contrary, the relationships with the air temperature and the solar radiation exhibit an exponential behavior. The coefficients of adjusted determination (R^2_{adj}) describing how well the regression lines or curves fit the set of data are also provided in Fig. 3 and demonstrate the goodness of most fits.

Despite the oxidation and volatilization processes can strongly control the concentrations of PAHs in the atmosphere during periods with different climatic and weather conditions, the role of biomass burning for agricultural purposes or for domestic heating is gaining an increasing attention for being recognized as a main source of PAHs in various European locations (e.g. Junninen et al., 2009; Sheesley et al., 2009; Bari et al., 2010; Poulain et al., 2011; Reche et al., 2012). As for the Northern Italy, van Drooge and Perez Ballesta (2009) estimated that wood burning can contribute from 30 to 70% of the PAHs in PM_{10} in semirural sites of Po Valley, whereas Belis et al. (2011) estimated that it may contribute with more than 75% of the BaP in the central Po Valley and near alpine valleys during winter. The significant role of this source in PAHs emissions is confirmed by the high PAHs mass ratios reached in winter mainly in Belluno and Feltre and, generally, in all the rural background sites (Fig. 2b). In these areas, the use of wood and softwood as an alternative fuel for home heating instead of the commonly used methane is higher than in other urban sites of Veneto and recent studies identified the biomass burning as the main source of PAHs in the Po Valley (Piazzalunga et al., 2013).

5.2. Spatial variations

Starting from the evidence that particulate phase PAHs have quite similar annual average values and seasonal trends in the whole region, an analysis of the inter-site concentration differences was conducted. Since the strong influence of oxidation and volatilization mechanisms in the warmest months causes a rapid drop of PAHs levels in the whole region between April and October (Supplementary material Fig. 2), the spatial variations were only calculated for the coldest semester (15 October–15 April). Moreover, the remote alpine site BL-RUR was excluded from the statistics because of the high number of samples below the LODs. Because the Shapiro–Wilk test applied to this new dataset revealed no normal distributions for PM_{10} and Σ_8PAHs at $p < 0.05$, the nonparametric Kruskal–Wallis analysis of variance by ranks was used to test the significance of inter-site variations. The test is based on the rank of each sample instead of its value and the null hypothesis assumes that the central values of the groups (medians) are equal, and is rejected for $p < 0.05$. Thus, the post-hoc Dunn's test for multiple sample comparison with a Bonferroni correction was performed to point out the sites which significantly differ in Σ_8PAHs levels. Table 4 shows the Kruskal–Wallis z-values (Siegel and Castellan, 1988) having $p < 0.01$, which highlight the pairs of sites having significant differences in Σ_8PAHs levels. The results show that most of the sites have similar PAHs concentrations during the cold period, but five sites present a larger number of significant z-values, and stand out from the

Table 4
Results of the Kruskal–Wallis analysis of the variance (bottom-left) and Spearman's rank correlations (upper-right) calculated for the Σ_8PAHs levels amongst sites.

	BL-URB	BL-SUB	TV-URB	VI-URB	VI-URB2	VR-URB	VR-SUB	VR-TRA	PD-RUR	PD-URB	PD-TRA	PD-IND1	PD-IND2	PD-IND3	PD-IND4	VE-RUR	VE-URB	VE-TRA	RO-RUR	RO-URB
BL-URB	–	0.90	0.87	0.83	0.76	0.79	0.79	0.90	0.76	0.72	0.79	0.77	0.78	0.71	0.79	0.90	0.87	0.85	0.78	0.84
BL-SUB		–	0.83	0.80	0.86	0.83	0.90	0.93	0.91	0.91	0.91	0.91	0.89	0.88	0.92	0.93	0.84	0.82	0.91	0.83
TV-URB			–	0.87	0.65	0.86	0.92	0.81	0.90	0.88	0.88	0.90	0.87	0.86	0.93	NC	0.91	0.94	0.84	0.88
VI-URB		4.33		–	0.80	0.83	0.77	0.91	0.85	0.87	0.90	0.84	0.87	0.83	0.88	0.77	0.81	0.87	0.83	0.82
VI-URB2		5.69			–	0.85	0.83	0.95	0.69	0.60	0.66	0.70	0.75	0.69	0.76	0.78	0.66	0.82	0.66	0.87
VR-URB		6.28				–	0.83	0.75	0.82	0.84	0.83	0.89	0.83	0.78	0.83	0.90	0.85	0.92	0.83	0.92
VR-SUB		6.16					–	0.86	0.90	0.82	0.89	0.86	0.89	0.84	0.84	0.90	0.74	0.85	0.87	0.87
VR-TRA	4.79	7.83	5.32					–	0.87	0.90	0.88	0.84	0.88	0.86	0.93	0.95		0.70	0.87	
PD-RUR					4.84	5.46	5.31	6.99	–	0.94	0.95	0.95	0.97	0.93	0.94	0.88	0.90		0.92	NC
PD-URB								5.54		–	0.98	0.96	0.96	0.95	0.92	0.90	0.94		0.86	NC
PD-TRA								4.73			–	0.96	0.97	0.95	0.93	0.90	0.94	0.95	0.89	NC
PD-IND1								4.91				–	0.96	0.95	0.90	0.94	0.94	0.95	0.90	NC
PD-IND2								4.19					–	0.96	0.93	0.88			0.90	NC
PD-IND3								5.06						–	0.92	0.88			0.87	NC
PD-IND4		6.71	4.49						5.96	4.63				4.17	–	0.96	NC		0.91	NC
VE-RUR		6.81	4.55						6.05	4.69		4.09		4.23		–	0.79	0.88	0.92	0.83
VE-URB		5.47							4.67								–	0.94		0.87
VE-TRA						4.05		5.64							4.68	4.76		–	NC	0.88
RO-RUR		6.06							5.20										–	NC
RO-URB		5.46							4.62											–

NC = no computable correlation.

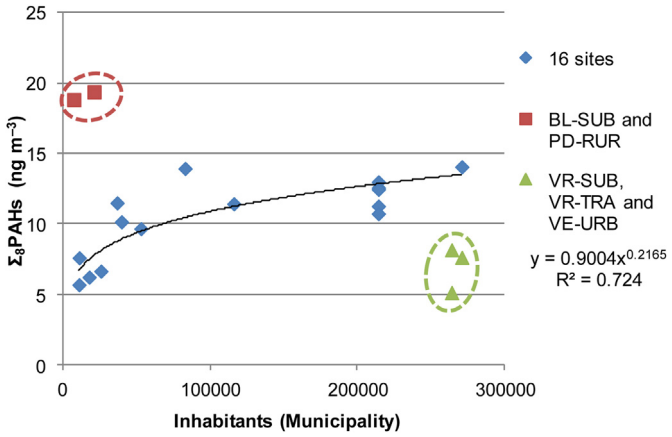

Fig. 4. Relationship between the number of inhabitant of the Municipality and the measured Σ_8PAHs concentrations in Veneto during the cold season.

others: VR-TRA, PD-IND4 and VE-RUR show significantly lower concentrations, whereas BL-SUB and PD-RUR significantly higher.

The spatial versus temporal relationships among the Σ_8PAHs levels measured in the sites were estimated by calculating the Spearman's rank correlations amongst sites. The correlations are also reported in Table 4 and show significant ($p < 0.01$) positive relationships for almost all sites. Only VE-URB and VE-TRA appear to be not significantly correlated with PD-RUR and the industrial sites of Padova. This analysis show that the PAH concentration values change simultaneously throughout the study area and points out that both the emission sources and the accumulation/removal processes in the atmosphere of the region.

Since large variations in population density in the region can be responsible of different levels of atmospheric pollution, an attempt to link the concentration of PAH with the number of inhabitants in the municipalities of the sampled areas was carried out. Fig. 4 shows the scatterplot of the number of inhabitants in a municipality and the measured concentrations Σ_8PAHs during the cold season. For sixteen sites a significant exponential relationship ($R^2 = 0.72$) is evidenced, but this relationship is not observed in five sites. In the two sites with the highest concentrations in the region (BL-SUB and PD-RUR) concentrations were about three times higher than in sites with an equal number of inhabitants per municipality. On the contrary, at the two sites of Verona and the site of urban background concentrations of Venice are about half those of municipalities with similar population size. Although this calculation can be directly influenced by the location of the site within the city environments and its different categorization, this result shows once again how BL-SUB and PD-RUR present anomalously high PAHs concentrations compared to the others. On the contrary, these results show that the concentrations of PAHs in Mestre-Venice and Verona are generally low in view of the resident population.

5.3. BaP toxic equivalent concentrations

The annual BaP equivalent values calculated in the selected 21 sites are presented in Fig. 5a. The annual regional average BaP_{TEQ} (average of all 3477 samples) was 1.7 ng m^{-3} and the congener most contributing to the total carcinogenic potential of the PAH mixture was BaP, with values (mean ± standard deviation) of 60 ± 13%. The second highest contributor was DBahA (14 ± 12%), followed by BbF (9 ± 3%), IP (6 ± 2%), BaA (5 ± 2%), BkF (4 ± 1%), whereas the other congeners contribution was ~1%. Similar contributions of BaP were found in other studies (e.g. Boström et al., 2002; Bari et al., 2010), confirming that BaP is a suitable indicator of carcinogenic potency of PAHs mixtures in ambient air. A comparison with BaP_{TEQ} levels reported in other studies is difficult because of different analytical methods and TEFs used. Moreover, also the selection of different congeners may result in incomparable values of the total toxicity. However, being hardly possible to quantify the uncertainties caused by the different methods used, we can only compare the data obtained. The values measured in Veneto appear lower than those reported for the urban Northeast Region of China (Li et al., 2011) and North-central part of India (Masih et al., 2010), but higher than those found in Europe: UK (Delgado-Saborit et al., 2011), Spain (Arruti et al., 2012) and Central Italy (Tuscany: Martellini et al., 2012). In conclusion, even considering the limitations in the use of BaP_{TEQ} approaches summarized

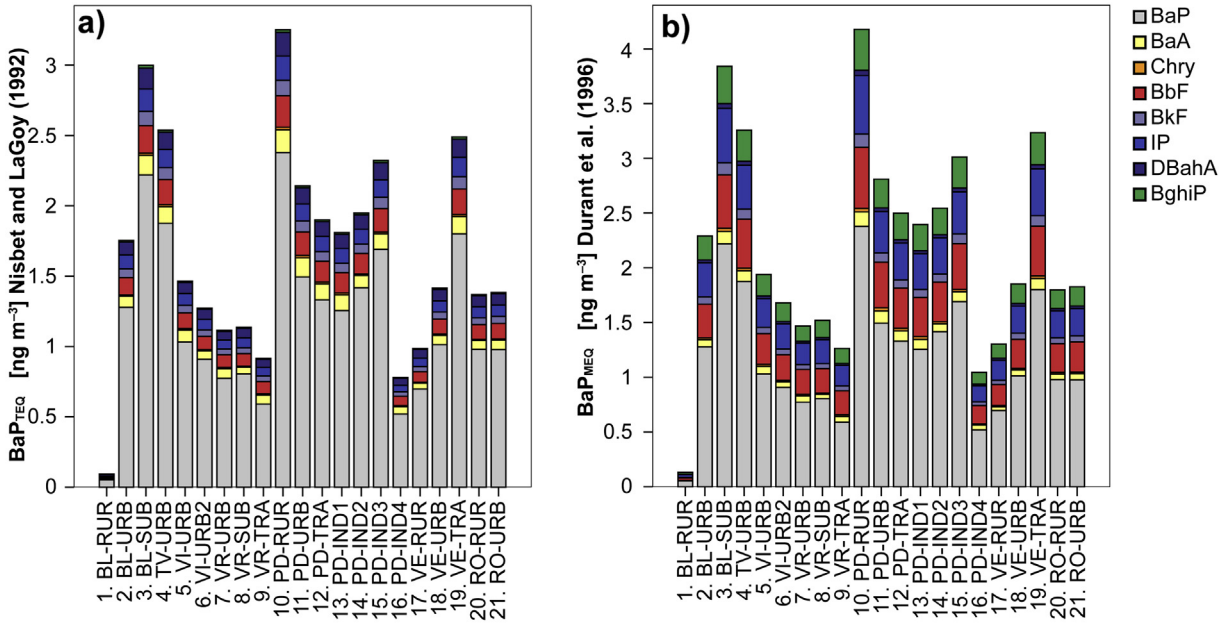

Fig. 5. BaP equivalent values calculated in the selected 21 sites.

in Supplementary material Table 4, the results show particularly worrying conditions for the whole Region, with 17 sites over the threshold value of 1 ng m^{-3}.

Similarly, the annual regional average BaP_{MEQ} was 2.2 ng m^{-3} (Fig. 5b) and the congener most contributing to the total carcinogenic potential of the PAH mixture was BaP (46 ± 9%), followed by BbF (17 ± 4%), IP (14 ± 3%), BghiP (12 ± 4%), whereas the other congeners contribution was <4%.

6. Conclusion

This study is the first one conducted in Veneto on a regional scale. Originally conceived as a concluding report after a number of papers focused on limited areas of the region it has produced some important information for decision makers. Results show that the air pollution caused by PAHs is relatively high in large part of the region: 10 sites exceeded the levels of BaP targeted by the European legislation and 17 breached this target when considering the BaP_{TEQ}. The seasonal pattern of PAHs was the same all over the region, with a marked increase of concentrations between October and November and a drop between March and April, in phase with the observed changes in air temperature and sunlight. The concentrations of PAHs were found directly proportional to those of other gaseous pollutants (CO, NO, NO_x, SO_2) suggesting a common polluting source and similar atmospheric processes. On the contrary, PAHs levels were inversely correlated to ozone, whose role in PAH oxidation mechanisms is well known.

A relevant result is that PAHs levels are very well correlated throughout the territory and most of sampling stations show very similar concentrations even if placed in differing environments. It can be concluded that the PAH air pollution in the Veneto is quasi-uniformly distributed throughout the region and the processes of emission and removal are similar. Considering that emission inventories for the Veneto show that non-industrial combustions (e.g., gas and oil boilers, wood and pellets fireplaces, cookers, woodstoves) account about for about two third of total PAHs emissions (ISPRA, 2012; Veneto Region, 2013), followed by waste treatment and disposal (16%), production processes (5%) and road transport (3%), measurement campaigns should be conducted in the future to better understand the contributions of those sources. In particular, some important aspects should be considered in further studies and in the implementation of future regulations as well:

1) As this study did not detect significant increases in PAHs in traffic or industrial sites and showed that higher levels can be reached far from direct anthropogenic sources, such as rural or suburban areas, the role of biomass combustions may play a very important role. The lack of existing regulations at both national and regional levels in the use and installation of fireplaces using wood or pellets it appears therefore an increasingly serious and underestimated issue for the pollution of the ambient air. It is advisable that the use of biomass combustion systems be regulated and the implementation of the best available technologies in all the regional territory be favored as well. In agreement with observations recently reported by the literature, this study also provides evidence of the importance of residential wood combustion in northern Italy, which has recently increased in place of more expensive fuels, such as oil or gas.
2) Possible actions to mitigate air pollution so far imposed at the local level, such as limiting the number of circulating vehicles on the basis of even or odd numbers of license plates, are bound to have poor effects if not extended to the region or the whole Po Valley. In the same manner actions to mitigate other relevant PAHs sources shall be extended simultaneously in the whole region.
3) Probably the whole monitoring system. I.e. the number of stations and their categorization deserve being revised. Finally, from the analysis of the territorial variations in two sites (PD-RUR and BL-SUB) anomalously high PAHs concentrations were recorded. These became even more evident by considering the population density as a surrogate for the potential anthropogenic influence.

Disclaimer

The statements and conclusions in this paper are those of the authors and not necessarily reflect the views of ARPAV.

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Appendix A. Supplementary data

Supplementary data related to this article can be found at http://dx.doi.org/10.1016/j.atmosenv.2013.07.025.

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