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CHEMISTRY IN A SUSTAINABLE SOCIETY

The impact of infield biomass burning on PM levels and its chemical composition

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Abstract In the South of Italy, it is common for farmers to burn pruning waste from olive trees in spring. In order to evaluate the impact of the biomass burning source on the physical and chemical characteristics of the particulate matter (PM) emitted by these fires, a PM monitoring campaign was carried out in an olive grove. Daily PM10 samples were collected for 1 week, when there were no open fires, and when biomass was being burned, and at two different distances from the fires. Moreover, an optical particle counter and a polycyclic aromatic hydrocarbon (PAH) analyzer were used to measure the high time-resolved dimensional distribution of particles emitted and total PAHs concentrations, respectively. Chemical analysis of PM10 samples identified organic and inorganic components such as PAHs, ions, elements, and carbonaceous fractions (OC, EC). Analysis of the collected data showed the usefulness of organic and inorganic tracer species and of PAH diagnostic ratios for interpreting the impact of biomass fires on PM levels and on its chemical composition. Finally, high time-resolved monitoring of particle numbers and PAH concentrations was performed before, during, and after biomass burning, and these concentrations were seen to be very dependent on factors such as weather conditions, combustion efficiency, and temperature (smoldering versus flaming conditions), and moisture content of the wood burned.

Keywords Biomass burning · PM10 · Combustion · Chemical characterization · High-time resolution · Optical particle distributions

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Introduction

Biomass combustion is an important source of atmospheric aerosols and greenhouse gases (Van der Werf et al. 2006; Bo et al. 2008; Omer and Ertugrul 2010; Urbanski et al. 2011; Reisen et al. 2013) worldwide. In recent years, atmospheric pollution from biomass burning has become an issue of public concern because of its effects on climate change, on atmospheric chemistry, and on human health (Verma et al. 2008; Alves et al. 2010). Extensive studies have shown that biomass combustion emits great quantities of the fine and ultrafine particles associated with increased morbidity and mortality. Ultrafine particles can penetrate deeply into the respiratory tract and can even cross biological barriers, leading to adverse effects on health (Brown et al. 2002; Nemmar et al. 2002; Ibald-Mulli et al. 2002; Nussbaumer 2003; Pope and Dockery 2006; Reisen and Brown 2006; Mazzoli-Rocha et al. 2010).

It is estimated that about 90 % of biomass combustion is due to human activities, and that only a small percentage of natural fires contribute to the total amount of vegetation burned. Numerous studies have shown the impact of biomass burning on local and regional air pollution in North America (Zhang et al. 2010; Dutkiewicz et al. 2011), Asia (Keywood et al. 2011; Reisen et al. 2013), and Europe (Saarikoski et al. 2007; Caseiro et al. 2009; Borrego et al. 2010; Yli-Tuomi et al. 2012), focusing attention on residential wood burning. This is an increasingly common popular alternative energy source to fossil fuels, and may have a negative effect on air quality. In winter, this wood smoke is an important local source of particles that can significantly contribute to the total particulate matter (PM) mass and/or organic aerosol fraction in rural and/or urban locations (Naeher et al. 2007). Several papers have evaluated the influence of biomass burning on PM levels in Europe; its contribution to the total PM1 organic fraction was estimated at approximately 37–68 % in the city of Grenoble (France), 35–40 % in urban Zurich (Switzerland), 79 %

in the city of Prague (Czech Republic). Moreover, biomass burning source contributed to approximately 50 % of the PM10 mass in southwestern Germany, to 10 % of PM2.5 in Vindingen (Denmark) and to 44–57 % of the total mass concentration in the size range 25–606 nm in Lycksele (Sweden) (Glasius et al. 2008; Krecl et al. 2008; Saarikoski et al. 2008; Bari et al. 2009; Favez et al. 2010; Lanz et al. 2010). In an overview of central European data, it was estimated that the percentages of aerosols emitted by biomass burning ranged from 17 to 49 % of total PM1 organic aerosols in winter (Lanz et al. 2010). In Italy, Pastorello et al. (2011) have reported the substantial contribution of wood burning to the emission inventory. For Italy's Apulia Region, Amodio et al. (2010) have shown that combustion processes account for 16 % of PM2.5, highlighting critical hot spots which greatly contribute to PM levels derived from wood smoke. In addition, variable factors, such as weather conditions, combustion efficiency, burning temperature (smoldering versus flaming conditions) and moisture contents of biomasses, create differences in the chemical composition and size distribution of particles emitted (Park et al. 2013; Zhang et al. 2013).

In South Italy, it is common for farmers to burn pruning waste from olive trees in spring. Despite controls by local authorities, biomass burning has a great impact on the levels and chemical composition of PM in nearby urban agglomerations. Olive groves are usually close to densely populated areas, and so, biomass burning may cause increased exposure to air pollutants in certain seasons, thus increasing potential risks for human health. Several authors (Oanh et al. 2005; Sillanpa et al. 2005; Hays, et al. 2005; Saarikoski, et al. 2007) have studied particulate emissions from sources such as wood-burning stoves and from wildfires. However, there is very little detailed information on the chemical composition and size distribution of aerosols emitted by the burning of agricultural waste (Andreae and Merlet 2001; Hays et al. 2005). Therefore, the main objective of this study was to carry out the chemical and physical characterization of PM10 aerosols from biomass fires. In detail, an assessment of the impact of these fires on the levels and chemical composition of PM10 in comparison with periods without any open fires was made. Tracer species and diagnostic ratios related to biomass burning source were identified. Finally, high time-resolved monitoring of the particle number and total polycyclic aromatic hydrocarbon (PAH) concentrations was performed in order to identify the main parameters affecting particle distribution and total PAH levels.

Materials and methods

Monitoring campaign strategy

PM10 samples were collected in an olive grove using a high-volume air sampler from April 1–6, 2012. The sampling site can be classified as a regional background or rural site because it mostly consists of olive groves and because there are no anthropogenic source emissions in the surrounding area. In order to assess the impact of biomass burning source on the levels and chemical composition of PM, PM10 daily samples were collected on days without open fires and also on days when biomass was being burned. In addition, a second high-volume air sampler was used to collect PM10 samples only during the 3 h when olive tree waste was being burned, and was positioned at two different distances from the fire. The PM10 samplers were placed 4 m from the bonfire for 1 day, and at a distance of 20 m on the other days. In all sampling days, the wind blew from the south and the sampler was downwind. Moreover, when PM10 samples were collected at 20 m from the source, high wind speed and wind gusts were registered, while lower wind speed was detected when PM samplers were located at 4 m from the source. Chemical analysis of PM10 samples was performed in order to identify inorganic components such as ions and elements, PAHs, and carbonaceous fractions (organic carbon (OC), elemental carbon (EC)). Finally, an optical particle counter (OPC) was used to determine the particle number concentration, and a PAH analyzer was used to measure the total PAH concentrations.

PM sampling and mass determination

PM10 samples were collected on quartz fiber filters (Whatman) using a high-volume air sampler (Tisch Environmental). As reported by UNI EN 1234-1, PM filters were conditioned before and after being weighed in a climatic chamber provided with a control system for the temperature and the humidity (20±1 °C and 50±5 % RH) (Activa Climatic, Aquaria, Milano, Italy). After this, an analytical balance (Sartorius series Genius, mod. SE2, Germany) with a sensitivity of 0.0001 mg was used to measure the particulate mass collected on the filter surface. Circular portions (47 mm diameter) of the high volume filters were then cut and analyzed in order to determine ions (Cl^-, NO_3^-, SO_4^{2-}, Na^+, NH_4^+, K^+, Mg^{2+},Ca^{2+}), elements (Al, Fe, Cu, Zn, and Pb), PAHs, and carbonaceous fractions (OC, EC).

Ion analysis

The ionic PM10 fraction was extracted by ultrasonic agitation of a quarter of the circular portion immersed in two 5-mL aliquots of deionized water for 20-min periods. A Dionex DX120 (Dionex, Sunnyvale, CA, USA) Ion Chromatography system equipped with an electrical conductivity detector was used to analyze anions, and a Dionex DX600 Ion Chromatography system was used to analyze cations. Anions were analyzed using a Dionex IonPac AS4A-SC column and an isocratic 1.8-mM sodium carbonate 1.7-mM sodium bicarbonate eluent, and cations were analyzed using a Dionex

IonPac CS12A column and an isocratic 20-mM methanesulfonic acid eluent (Amodio et al. 2010).

Element analysis

The elemental composition (Al, Ca, Cr, Co, Cu, Fe, Pb, Mg, Mn, Mo, Ni, K, Na, Sr, Ti, V, Zn) of PM10 was determined by inductively coupled plasma atomic emission spectrometry, after one fourth of the filter had been acid digested in 8-ml nitric acid and 2-ml hydrogen peroxide solution, according to EN 14902:2005. Acid digestion was carried out in a microwave system (Milestone mod. Ethos D) that reached approximately 180 °C within 20 min (500 W), increased the temperature slowly to approximately 220 °C and then maintained this temperature for about 20 min (500 W). Daily calibration standards were used for quantification and the quality control of the analytical procedure and the determination of the recovery percentage were carried out according to EN 14902:2005.

Polycyclic aromatic hydrocarbon analysis

The extraction of PAHs was performed by placing one half of the circular filter in a mixture of acetone/hexane (1:1) in a microwave-assisted solvent extraction system (Milestone, model Ethos D). The extracted samples were then analyzed using an Agilent 6890 PLUS gas chromatograph (Agilent Technologies, Inc., Santa Clara, CA, USA) equipped with a programmable temperature vaporization injection system and interfaced to a triple-quadrupole mass spectrometer, operating in electron impact ionization (Agilent MS-5973 N). Benzo[b]fluoranthene (BbF), benzo[j]fluoranthene (BjF), benzo[j]fluoranthene (BkF), benzo[a]pyrene (BaP), benzo(a)anthracene (BaA), indeno[1,2,3-cd]pyrene (Ip), dibenzo(a,h)anthracene (DBA), and benzo[g,h,i]perylene (BgP) were determined using perylene-D12 (PrD) as the internal standard, according to the methodology described by Bruno et al. (2007). The assessment of the performance and reliability of used methodology in terms of LOD, repeatability, and recovery percentage are also presented in the aforementioned paper.

Carbonaceous PM10 analysis

The carbonaceous fraction of PM10 was detected using an organic/elemental carbon aerosol analyzer (Sunset Laboratory Inc., Tigard, OR, USA). Rectangular punches (normally 1.50 cm^2) of PM10 filters were analyzed to detect OC and EC on the basis of a validated thermal optical method and following the NIOSH protocol. The speciation of organic and elemental carbon was achieved in controlled temperature and atmosphere conditions. He–Ne laser light passing through the filter allows continuous monitoring of filter transmittance, while an optical feature allows correction of the pyrolitically generated OC. Evolved carbon was quantified using a flame ionization detector and instrument calibration was achieved through injection of a known volume of methane into the sample oven (Birch and Cary 1996).

Particle and total PAH monitoring

During the monitoring campaign, an OPC was used to determine the numerical particle concentration and a PAH analyzer was used to determine the total PAH concentrations. To be more precise, an OPC Multichannel Monitor (FAI Instruments, Rome, Italy) was used in order to characterize the temporal trends of the particulate distribution. This instrument measures number concentrations of aerosol particles with optical diameters greater than 0.28 μm (32 size ranges) by means of eight optical channels with 1-min time resolution. The total PAH concentrations with 10-s time resolution were determined using a photoelectric aerosol sensor (PAS), denominated EcoChem PAS 2000 Analyzer (EcoChem Analitycs; USA).

Results and discussion

Figure 1 shows PM10 mean concentrations registered on days when biomass burning occurred (event, 24 h) and days when no burning took place (no event, 24 h). Mean PM10 concentrations on event days were about twice the concentration detected on no event days. PM10 samples collected only during the hours when olive tree waste was being burned (event, 3 h) and at different distances from the fire (20 and 4 m) presented concentrations two orders of magnitude greater than the concentrations measured in no event conditions. Moreover, the PM10 concentrations measured on the filters collected only during biomass burning events at 4 m from the source were twice the concentrations measured when the sampler was placed at 20 m from the source. This finding confirmed that distance from the source is an important factor affecting PM10 levels.

Chemical characterization of the collected samples made it possible to obtain the levels of the major organic and inorganic components (see Table 1). The concentrations and the chemical composition of PM10 samples obtained in this study were also compared with data from previous monitoring carried out at an urban site in Bari (Apulia Region) (Amodio et al. 2012). As shown in Table 1, the highest OC concentrations were found in the samples collected during 3-h combustion, especially when PM10 was collected 4 m from the source. Moreover, OC concentrations during event conditions were 347 μg/m^3 (at 20 m) and 1,354 μg/m^3 (at 4 m), respectively, 60 and 250 times the OC concentrations registered in the urban area (5.4 μg/m^3). The EC concentrations did not increase as much

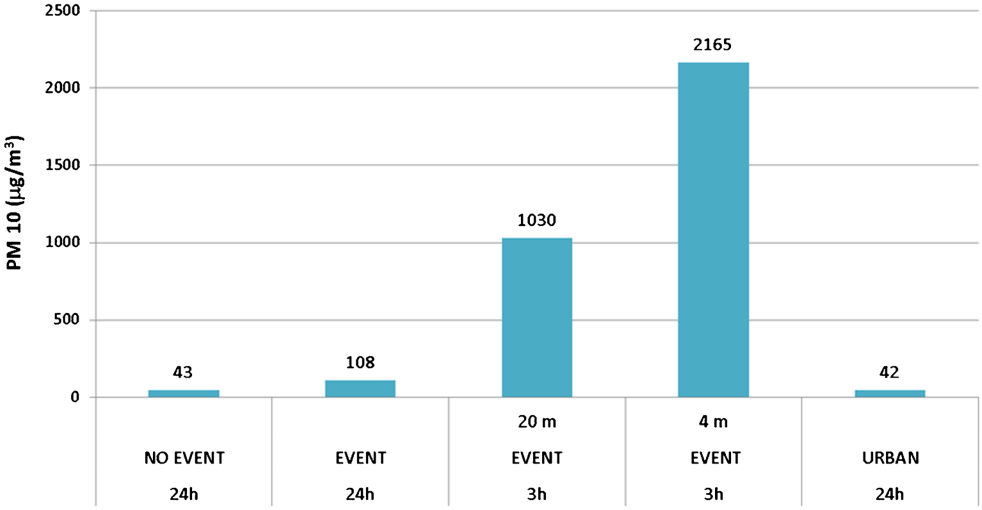

Fig. 1 PM10 concentrations (microgram per cubic meter) determined in event (24- and 3-h samples) and no event conditions at 4 and 20 m from the biomass fire

as the OC concentrations during event conditions, so that we observed a noticeable difference for the OC/EC ratio. OC/EC ratios provide useful information on the varying nature of combustion sources and their strength, especially biomass burning in comparison with fossil-fuel emissions (Rengarajan et al. 2007; Ram et al. 2008). OC/EC ratios reflect the differences in the intensity and in the type of emission sources because EC is traditionally a fossil-fuel combustion marker. In this study, traffic was excluded as an emission source because of the OC/EC ratios, especially during events and was higher than the values registered at the urban site. Moreover, the lower levels of EC could be due to fire intensity and to the biomass type (Robinson et al. 2011). Zhang et al. (2013) showed that higher temperatures of flaming phase burning produced more soot (EC), than smoldering-type combustion and that lower EC concentrations were also determined when greener fuel types burning occurred (e.g., stubble, green leaves, and branches).

Table 1 Pollutant concentrations in event and no event conditions

	No event	Event 24 h	Event 3 h 20 M	Event 3 h 4 M
µg/m^3				
PM10	43	108	1,030	2,165
ng/m^3				
BaA	0.19	64	508	988
BjF	0.18	79	529	611
BbF	0.19	50	528	611
BkF	0.19	26	172	211
BaP	0.20	76	533	730
DBA	0.13	19	123	167
IP	0.20	72	474	529
BgP	0.05	65	428	471
µg/m^3				
OC	4.9	55.8	347	1,354
EC	0.7	1.8	20	41
Na^+	2.9	1.53	19	2.8
NH_4^+	0.4	0.02	0.5	0.30
K^+	0.4	11	84	46
Mg^{2+}	0.4	0.1	1.9	0.6
Ca^{2+}	1.6	1.3	11	5.5
Cl^-	2.5	6.5	64	9.8
NO_3^-	3.0	1.71	9.3	4.4
SO_4^{2-}	5.1	7.5	45	31
Al	1.0	1.2	8.6	3.3
Fe	0.8	0.9	5.9	1.7
Zn	0.1	0.5	0.6	0.6

The PAH concentrations on event days were almost two orders of magnitude higher than the concentrations on no event days (see Table 1). The high PAH concentrations, particularly of BaP, suggested that biomass fires of this kind may constitute a public health hazard, especially for the farmers who carry out seasonal burning in order to eliminate waste and to fertilize their fields. Moreover, it is important to consider that Directive 2004/107/EC (adopted 31.12.2012) imposes on all European Union member states a maximum value of 1 ng m^{-3} for the total BaP content of PM10 averaged over a calendar year. BaP was selected because it is carcinogenic and because it is considered a good indicator of the total PAH content in the atmosphere. However, an annual value may be not useful enough to indicate the real human exposure to PAH inhalation, especially during hot spot events. Taking into account the PAH concentrations in mainstream and sidestream cigarette smoke, it is possible to evaluate how many cigarettes an olive grove worker would need to smoke in order to be exposed to the same load of PAHs. For example Moir et al. (2008) and Lee et al. (2011) determined that smoking one cigarette released 91 and 70 ng of BaP, respectively. When these values are compared with the values determined in this work for biomass burning, it is possible to conclude that workers in olive groves where pruning waste is being burned are exposed to sidestream smoke equivalent to about 85 cigarettes. Moreover, other papers have reported BaP concentrations ranging from 5 to 15 ng for one cigarette mainstream smoke (Smith et al. 2001; Rustemeier et al. 2002; Moir et al. 2008), suggesting that the biomass burning corresponds to the mainstream smoke of about 500 cigarettes during 3 h.

As shown in Figs. 1 and 2, the mean of daily PM10 concentrations and the percentage composition of chemical pollutants were broadly similar both at the background site in no event conditions and at the urban site. In particular, the potassium percentage was 0.8 % at the regional background site and 1.0 % at the urban site. The PAH percentages were the same at both sites, whereas the percentages of the typical traffic marker EC were lower at the background site than at the urban site. These findings suggest that there was an additional source at this background site, but not traffic, that caused the increased PM10, K^+, and PAH concentrations. These unexpected results were probably due to the burning of olive tree waste in the surrounding fields, because this is still a common practice in South Italy. The sampling period (March and April) was selected deliberately, because this is when farmers finish pruning their olive trees and then burn the waste. Comparing event (24 h) and no event conditions, it was observed that OC, K^+, and PAHs percentages during biomass burning were about 4, 10, and 100 times higher, respectively, than OC, K^+, and PAHs percentages measured in no event conditions. This result was also confirmed when taking into account the PAH, OC, and K^+ percentages determined by 3-h sampling during biomass burning. This finding confirmed the importance of these species as markers of the biomass burning source (Viana et al. 2008; Huang et al. 2010). Wood combustion is known to be an important source of organic carbon and PAHs produced by the pyrolysis of cellulose and lignin, and of potassium, an earth element found in the core of smoke particles (Posfai et al. 2003; Mandalakis et al. 2005; Dhammapala et al. 2007). When a comparison was made of the percentages obtained from 3-h sampling at different distances from the biomass fire, it was found that PAH percentages remained almost constant, while OC percentages increased when the sampler was nearer to the source (62 %). On the contrary, the K^+ percentage in event samples (3 h) collected at 4 m from the source was slightly lower than the K^+ percentage in samples collected at 20 m. This was due to the difference in atmospheric conditions. There were high wind speeds on the event days when PM10 samples were collected at 20 m from the source; therefore crustal resuspension caused higher magnesium, calcium, and potassium concentrations than the concentrations found in PM10 samples collected at 4 m from the source.

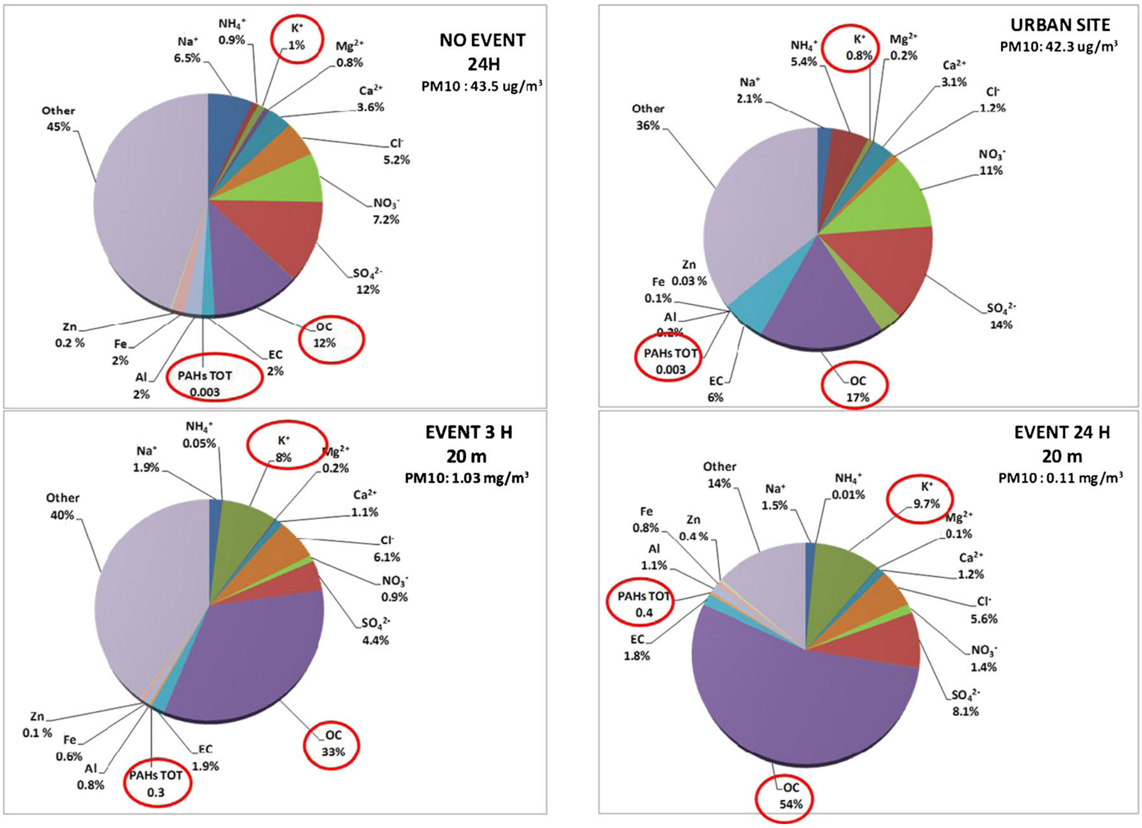

Fig. 2 Percentage composition of PM10 at background site during no event (**a**) and event conditions

These results were similar to those of Reid et al. (2005), namely that OC accounts for about 60 % of fresh dry smoke particles and that biomass burning performance and atmospheric conditions also influence the chemical composition of particulate matter (Adler et al. 2011; Gonçalves et al. 2011; Oanh et al. 2010).

In addition, Fig. 3 shows the percentage of each PAH in comparison with the overall mass of PAHs detected in event and no event conditions; BgP, BaA, and BaP percentages are higher in event conditions (24 h) than in no event conditions. Although it is well known that BaP is the major marker of combustion processes, in this study, it was found that other PAHs such as BgP and BaA increased during biomass burning. In fact, the experimental data revealed BgP percentages ranging between 4 % in no event conditions and 14 % in event conditions, while BaP and BaA percentages increased slightly. In addition, BaA percentage accounts for 23 % for the sample collected in 3 h during biomass burning and when the sampler was placed 4 m from the bonfire. Recent studies have reported characteristic BaP/BgP and IP/[IP + BgP] ratios of 1.4–2.0 and 0.64, respectively, during rice straw burning (Viana et al. 2008; Huang et al. 2010). Other authors have also reported that BaP/BgP and BaP/IP diagnostic ratios are strongly related to wheat residue burning in an experimental chamber (Hays et al. 2005). These values are reported in Table 2, and compared with those found during this study and with those specified in the NIST report for urban dust. All diagnostic ratios determined for the burning of olive tree biomass were higher than those determined for urban dust. In particular, the IP/BgP, BaP/BgP, and BaP/IP ratios registered in this study were about twice the ratios observed for urban dust; on the contrary IP/[IP + BgP] ratios for the samples collected during biomass burning and in urban areas are quite similar: 0.53 and 0.43, respectively. There was a good agreement between the

Table 2 Diagnostic PAH isomers ratios in this and other studies including NIST SRM-1649

	Urban dust NIST, SRM-1649b[a]	This study Event	Chamber experiment WHEAT—residues[b]	Other study
IP/BgP	0.75	1.12	1.28	–
IP/(IP + BgP)	0.43	0.53	0.55	0.64[c]/0.59[d]
BaP/BgP	0.63	1.55	1.43	1.4–2[c]
BaP/IP	0.83	1.38	1.22	–

[a] NIST report

[b] Hays et al. 2005

[c] Viana et al. 2008; Yang et al. 2010

[d] Gonçalves et al.2011

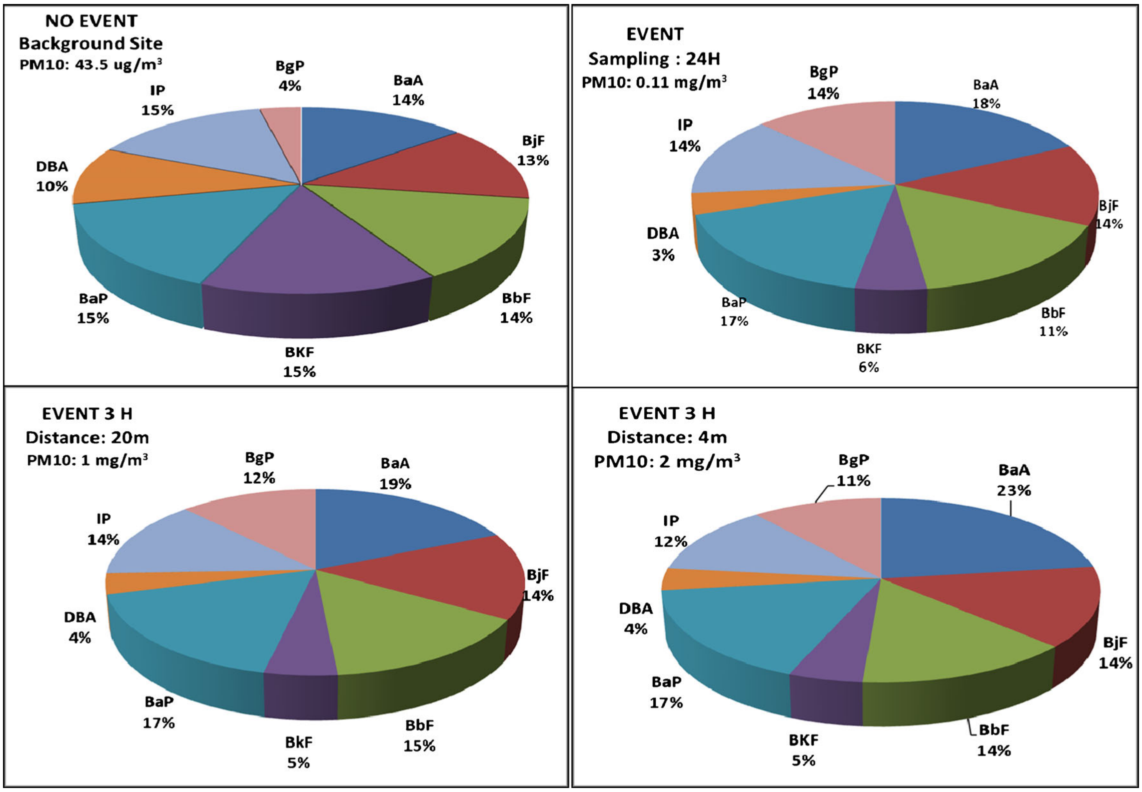

Fig. 3 PAH percentage composition measured during no event and event conditions

diagnostic ratios obtained in this work and the ratios obtained in an experimental chamber, and also with the values reported by other authors. Moreover, no significant differences were observed between the diagnostic ratios associated with the selected biomasses: olive tree residues (this study), rice straw residues (Viana et al. 2008 and Yang et al. 2010), wheat residues (Hays et al. 2005), and olive wood (Gonçalves et al. 2011). However, these findings suggest that the IP/[IP + BgP] diagnostic ratio is not a very useful tool for discriminating between urban and biomass combustion sources, because their characteristic values for diesel exhaust (0.43) and for biomass burning emissions (0.5–0.6) are too close. Anyway it's important to highlight that, even if the PAHs sampling has been conducted close to the source, the presence of some strong oxidants, such as OH, NO_2, and O_3, may affect the diagnostic ratios by oxidizing the more reactive congeners, resulting in a shift of the diagnostic ratios (Dvorská et al. 2011; Katsoyiannis et al. 2011). In fact, as reported in a previous study, the diagnostic ratio validity is based on source specificity and species conservation (Galarneau 2008).

Table 3 reports the event to no event ratios of the detected chemical species concentrations. These ratio were calculated considering the nanogram of each species with respect to PM mass (in milligram) for the considered samples (ngX/mgPM). As reported by Viana et al. 2008 and Huang et al. 2010, the chemical species can be considered enriched if the ratio is greater than 2, indicating that the event considered has made an important contribution to PM concentration. As expected, high event to no event ratios were determined for K$^+$, OC, and PAHs. Moreover ratio higher than 2 were also observed for chloride (Cl^-) in the biomass burning sample collected 20 m from the fire and for zinc (Zn) determined on samples collected over 24 h. Chloride has been identified as one of the elements emitted by biomass combustion together with K$^+$ (Jaffrezo et al. 1998), while the Zn detected was probably due to bioaccumulation of these metals in olive trees.

Table 3 Event/no event ratios determined on samples collected during 3 and 24 h at 4 and 20 m away from biomass burning source

	$\frac{\text{EVENT 3H}}{\text{NO EVENT}}$ 4 M	$\frac{\text{EVENT 3H}}{\text{NO EVENT}}$ 20 M	$\frac{\text{EVENT 24H}}{\text{NO EVENT}}$ 20 M
BaA	105	113	150
BjF	68	125	180
BbF	64	117	124
BkF	22	38	54
BaP	71	709	155
DBA	25	38	56
IP	53	101	146
BgP	204	390	566
OC	5.5	3.0	4.8
EC	1.2	1.2	1.1
Na^+	0.02	0.3	0.2
NH_4^+	0.02	0.1	0.02
K^+	2.1	8.1	9.8
Mg^{2+}	0.0	0.2	0.1
Ca^{2+}	0.1	0.3	0.3
Cl^-	0.1	2.1	1.0
NO_3^-	0.03	0.1	0.2
SO_4^{2-}	0.1	0.4	0.7
Al	0.1	0.4	0.6
Fe	0.1	0.4	0.6
Zn	0.1	0.3	2.2

The ratio were calculated starting from ngX/mgPM values for each species

It is well documented that the distribution and abundance of biomass burning aerosols are strongly dependent on combustion temperature (smoldering versus flaming conditions), aeration, burn duration, combustion efficiency, and a high moisture content of the wood burned (Simoneit 2002; Rajput et al. 2011).

High-resolution monitoring was performed in order to carry out a detailed investigation of these variables affecting the emissions from biomass burning, and this involved monitoring the number concentration of particles and total PAH concentrations before, during, and between two open fires. Figure 4 shows a noticeable difference between event and no event conditions. In addition, higher concentrations were found during the second biomass burning event, and this is probably related to the different dispersive capacity of the atmosphere and to the difference in burning characteristics.

Figure 4 shows that there was a difference in temporal behavior for number concentrations of finer particle and total PAH concentrations between the two events, considering only the hours when biomass burning was observed. In fact, the number of particles with a diameter of less than 0.28 μm and the total PAH concentrations showed a modulate trend in the first event, while in the second event, these concentrations were continuously high, and a less-defined modulation was observed (Fig. 5). These findings could be explained by the fact that flaming and smoldering phases alternated continuously during the first burning event, while during the second event, the source was continuously in the flaming phase and the temperature was constantly high. In addition, the wood in the second burning event had a high moisture content, thereby determining higher particle number and PAH concentrations, according to Rajput et al. (2011). These results indicate that the performance of the biomass burning process probably plays a

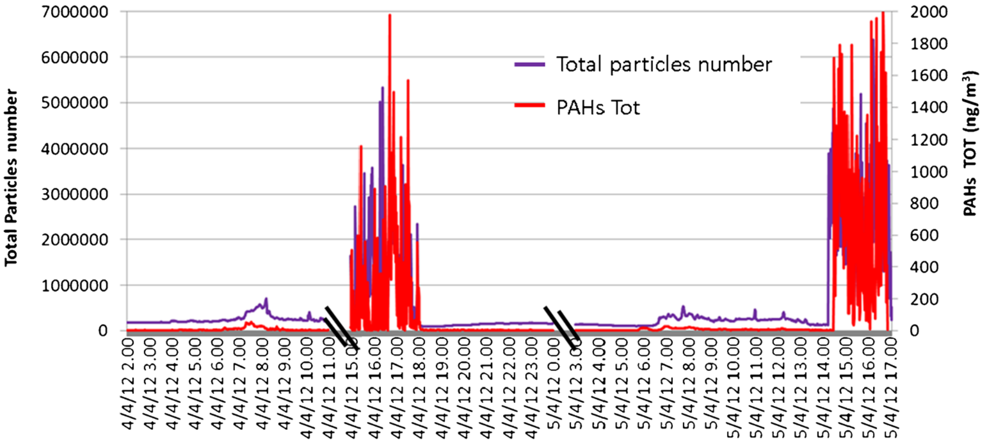

Fig. 4 Total particle number concentrations and total PAH concentrations before, during and after biomass burning

key role in determining the physical and chemical properties of emitted particles. It is well documented that the distributions and abundances of the biomass smoke constituents are strongly dependent on combustion

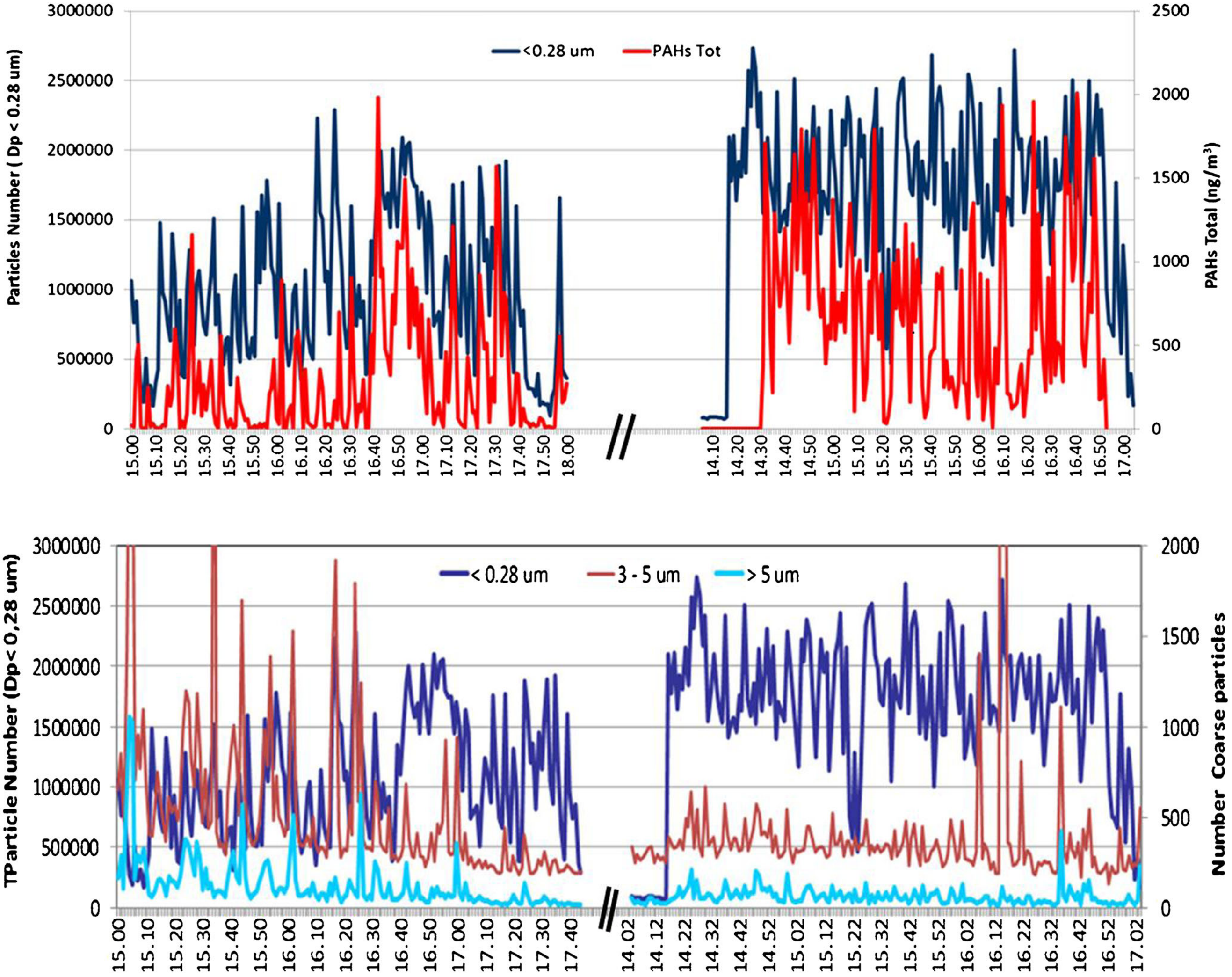

Fig. 5 Particles (Dp<0.28 mm) number concentrations and total PAHs (**a**); Particle number concentrations (Dp<0.28 mm; 3 mm<Dp<5 mm; Dp> 5 mm) (**b**) during two biomass burning events

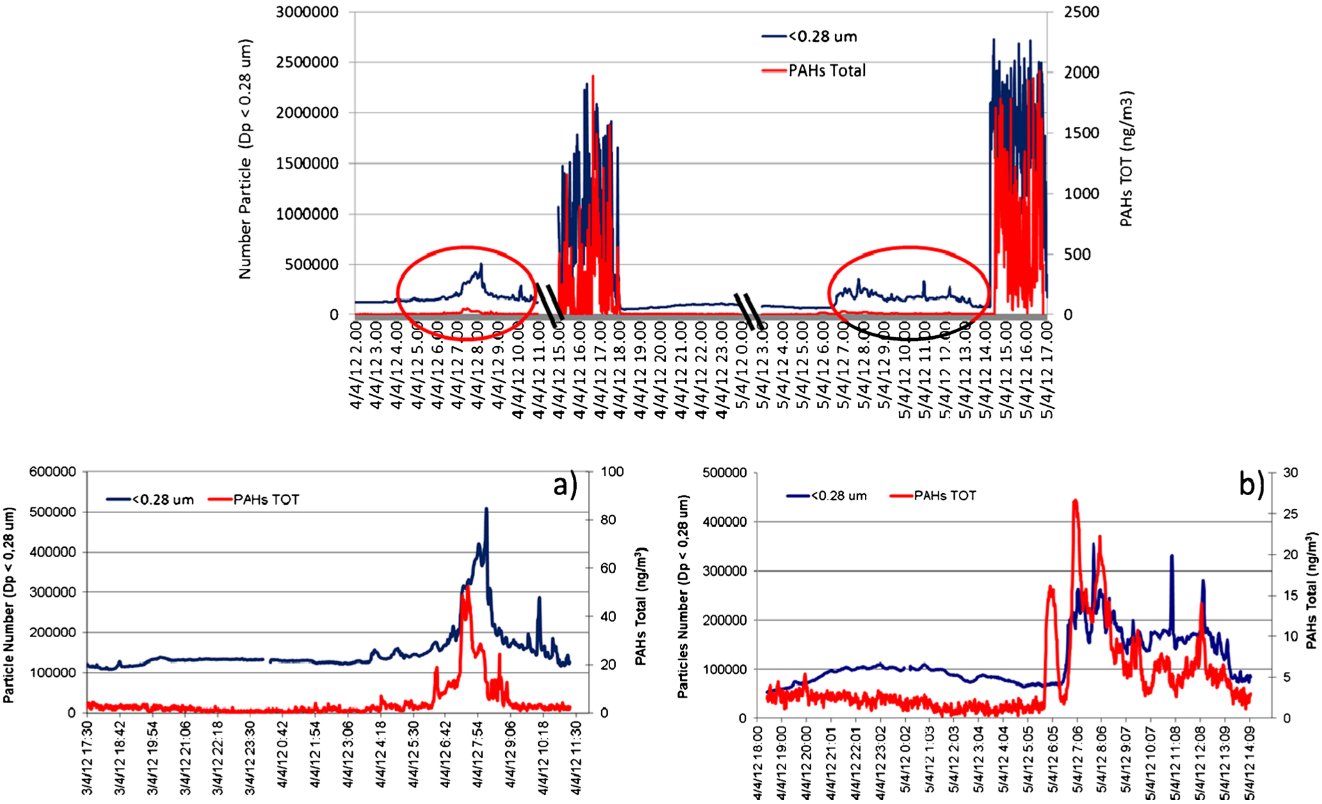

Fig. 6 Particle (Dp<0.28 mm) number concentrations and Total PAH concentrations before (zoom in **a**), during and after biomass (zoom in **b**) burning

temperature (smoldering versus flaming conditions) and efficiency, burn duration, and high moisture content of the wood (Simoneit 2002; Rajput et al. 2011).

The first burning event was also characterized by higher coarse particle number concentrations than those monitored during the second burning event, when finer particles prevailed, as it is possible to observe in the second section of Fig. 5. This finding is probably due to different atmospheric conditions, because high wind was recorded during the first event, causing many coarse particles to be soil resuspended.

Finally, as highlighted by Rajput at al. (2011), higher PAH concentrations found after the biomass burning process are due to emissions during the smoldering phase. Moreover, given that biomass burning ended in the evening and that the atmosphere usually has a lower dispersive capacity during the night, higher particle numbers and total PAH concentrations were expected in the hours immediately after the combustion process. However, this study found high concentrations of fine particles and total PAHs in the early hours of daylight and on different days (see Fig. 6). This evidence confirms the hypothesis that there were other anthropogenic sources in the surrounding area. Traffic should be excluded as a source, because the urban area is too far from the sampling site. Fine particle numbers and PAH concentrations probably increased because of other biomass burning sources near the sampling area, confirming that it is still common in South Italy for farmers to burn olive tree waste in spring.

Conclusions

This study showed the impact of burning olive tree waste on the levels and chemical composition of PM10. In order to characterize biomass burning sources, a monitoring campaign was carried out in an olive grove and the chemical characterization of PM10 samples collected was performed. High PM10, K^+, PAH, and OC concentrations were registered during biomass burning event, identifying these pollutants as biomass burning source markers. The high PAH concentrations suggested that fires of this kind may create a public health hazard, especially for farmers who burn biomass on a seasonal basis in order to eliminate waste and to fertilize their fields. This study also highlighted that the BaP/BgP, IP/BgP, and BaP/IP diagnostic < 0.28 function better than the IP/[IP + < 0.28] ratio in discriminating between two PAH emission sources, such as diesel exhaust and biomass burning. Finally, high-resolution monitoring of particle numbers and PAH concentrations was performed before, during and after biomass burning, and highlighted that these concentrations were strongly dependent on factors such as weather conditions, combustion efficiency and temperature (smoldering versus flaming conditions) and on the moisture content of the wood burned.

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