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Markers and influence of open biomass burning on atmospheric particulate size and composition during a major bonfire event

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HIGHLIGHTS

- Chemical and granulometric characterization of PM to provide bonfire tracer species.
- Combustion markers demonstrate that bonfires highly contribute to airborne PM.
- Lead and aluminum concentration increases, probably due to their bioaccumulation.
- Lvg, OC, PAHs, Al and Pb can be used together as specific markers of bonfires.

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ABSTRACT

This study aims to characterize PM from the open burning of bonfires as well as detect a series of useful tracer species for source apportionment studies. Total suspended particulate (TSP), PM_{10} and $PM_{2.5}$ were collected before, during, and after St. Joseph's Eve (18th of March). On this day, several bonfires are lit throughout the study area. Levoglucosan (Lvg), OC, EC, PAHs, soluble ions, and some metals (Al, Cd, Cu, Ni, and Pb) have been determined in each fraction.

Results show that the contamination of the area is similar to what is generally found in suburban areas. The fine fraction makes the highest contribution to PM. This fraction is mainly related to compounds composing the PM secondarily formed, while the coarser fractions are associated with natural matrices.

The bonfire event is an important source of particulate. All the combustion markers determined in $PM_{2.5}$ (EC, OC, PAHs (except for Flu and Pyr), K^+, Cl^-, and Lvg) register a higher concentration. Lvg/OC ratio confirms higher wood smoke emissions during these days. Both the concentration and the compound profile indicate a different origin of PAHs in the atmosphere. The highest concentration of K^+ and OC in TSP confirm the contribution of open fire, as well, to this fraction, which can be ascribable mainly to combustion ash. Nitrates and sulphates also show a higher concentration in the PM_{10}-TSP fraction. Surprisingly, there is also an increase in the concentration of components not usually considered combustion markers, i.e. Pb and Al in $PM_{2.5}$. This is probably ascribable to their bioaccumulation. In conclusion, Lvg, OC, PAHs, Al, and Pb can be used together as specific markers of bonfires to identify this source of particulate matter.

Abbreviations: Lvg, Levoglucosan; Flu, Fluoranthene; Pyr, Pyrene; B(a)A, Benz[a]anthracene; Cri, Chrysene; B(b)F, Benzo[b]fluoranthene; B(k)F, Benzo[k]fluoranthene; B(a)P, Benzo[a]pyrene; D(a,h)A, Dibenz[a,h]anthracene; B(g,h,i)P, Benzo[ghi]perylene; I(1,2,3)P, Indeno[1,2,3-cd]pyrene.

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1. Introduction

Among the several natural and anthropogenic sources of atmospheric aerosol, there is a growing attention to the biomass burning processes, which include the residential burning of wood or pellets for household heating, and open fires, such as agricultural debris burning, prescribed fires, forest fires, and bonfires (Lemieux et al., 2004). Biomass burning is becoming a topic of great concern among environmental matters, because it is difficult to control and because it locally produces a considerable quantity of pollutants. Among these particulate matters, with a high proportion of submicron particles (PM_1), and products of incomplete combustion, which have negative effects on human health, i.e. OC, volatile organic compounds, soot, PAHs, and polychlorinated dibenzodioxins (Nussbaumer, 2003; Piazzalunga et al., 2013).

Open fire encompasses a wide variety of activities. Some markers are characteristic of combustion processes, and are thus emitted by all open fires. Other markers depend on the kind of biomass burnt. In the literature, studies can be found which focus on the burning of agricultural debris, such as rice straw (Lee et al., 2008; Viana et al., 2008), barley straw (Ryu et al., 2007), wheat stubble (Mittal et al., 2009), wax apple (Lin et al., 2012), agricultural waste (Park and Cho, 2011), leaves (Schmidl et al., 2008a), and prescribed fire (Mazzoleni et al., 2007). Open fires may also be lit for recreational activities such as bonfires. Studies focusing on this activity especially concern the UK, where Bonfire Night is celebrated every year on the 5th of November, with large firework displays and the lighting of large bonfires (Agus et al., 2008; Colbeck and Chung, 1996; Dvke et al., 1997; Farrar et al., 2004; Harrad and Laurie, 2005). Nevertheless, these works concentrate on only a particulate fraction, while the number of chemical species determined is limited. Therefore a more comprehensive study is necessary.

In the province of Rimini (Italy, 534 km^2), on St. Joseph's Eve (18th of March), several flaming bonfires, called "fogheracce", are usually lit throughout the area, as a ritual to welcome spring.

Together with several large-scale public events, many individual households light their own bonfires, especially in the rural area. In this last case, the composition of the materials making up the bonfires is not well known; however pruning residues (especially of olives, vineyard and orchard) or other residues, originating from households' fields, are traditionally burnt, as for the public bonfires.

The impact of this event is of relevance beyond the study area, as similar events are common in many other countries (e.g. July 4th in the United States, "Bonfire night" on November 5th in the United Kingdom). Whilst these celebrations do not constitute a major everyday source of pollution, they can produce significant short-term increases in pollution when they do occur, emitting trace gases and dense clouds of smoke into the atmosphere, causing short-term degradations in air quality (Agus et al., 2008). Consequently, when "fogheracce" are lit, participants can be exposed to high particulate levels. This is demonstrated by the PM_{10} air concentration registered in the town of Rimini by the regional environmental protection agency (ARPA Emilia Romagna). PM_{10} concentrations on these days are well above the limit set out in the 2008/50/EC directive (50 $\mu g\ m^{-3}$), in 2009 and 2010 they ranged between 95 and 151 $\mu g\ m^{-3}$. St. Joseph's Eve therefore provides a unique opportunity to study the impact of biomass derived emissions on the atmospheric loading and size distribution of particles.

In this study, a sampling campaign was carried out in the suburban area of the city of Riccione (Rimini, Italy) before, during, and after St. Joseph's Eve. Total suspended particulate (TSP), PM_{10}, and $PM_{2.5}$ were collected and Lvg, OC, EC, PAHs, soluble ions, and some metals have been identified in each fraction. The aim of the study was to demonstrate, through the chemical characterization, that there is an important airborne particulate matter contribution due to bonfires and find new emission source markers, other than the well-known ones such as levoglucosan or water soluble potassium (Zhang et al., 2010). These tracer species will aid in the future identification of this type of PM episodes in other source apportionment studies in areas with similar biomass burning emissions.

2. Material and methods

2.1. Sampling site

The sampling site is located in a city park, on a 60 m above sea level hill ridge, in the southwestern suburban area of the medium-sized tourist town of Riccione (RN) (35,000 inhabitants) (Fig. 1). The site is alternately downwind of the costal urban area and of the hinterland, which is mainly characterized by the presence of an artisan district, a Municipal Solid Waste Incinerator (MSWI) and a motorway. The MSWI is 2 km away from the sampling site. It is authorized to burn 140,000 t of urban and hospital solid waste per year (maximum 1000 t $year^{-1}$ of the latter), and the emission stack is 40 m tall. The A14 motorway is about 600 m away and runs roughly 30 m below the sampling site. It is used by an average of 60,000 vehicles per day.

2.2. Sampling

The sampling campaign both of TSP and of the subfractions PM_{10} and $PM_{2.5}$ started on the 9th of March and ended on the 8th of April, 2011. Each sampling episode lasted 48 h. A total of 39 samples were collected, 13 for each fraction.

Two medium-volume samplers (Skypost PM, TCR TECORA) – one equipped with a PM_{10} sampling head, the other with a $PM_{2.5}$ sampling head – were used. Each sampler operated at a flow rate of 38.33 L min^{-1}. The characteristics of these samplers fulfill European Method CEN EN 12341 and US EPA Law 40 CFR Part 50. In addition to these, a third sampler (ECHO HiVol, TCR TECORA), operating at a flow rate of 200 l min^{-1}, was used for the collection of TSP.

2.3. Analysis

$PM_{2.5}$ and PM_{10} samples were collected on 47 mm quartz fiber filters, while TSP on 102 mm quartz fiber filters (MUNKTELL). To determine the ambient concentration of PM_{10} and $PM_{2.5}$, reference methods were the European Standard EN 12341 and 14907, respectively. After PM quantification, each filter was split into parts for the different chemical species determination:

$^1/_4$: OC and EC (1 cm^2 filter punch), the remaining part for ions
$^1/_8$: Lvg
$^3/_8$: Polycyclic Aromatic Hydrocarbons (only for TSP)
$^1/_4$: metals

The subsample dimensions were chosen on the basis of both expected air concentration of the different chemical species, and the quantification limits of the analytical methods.

Details of all the analysis techniques, of PM determination, and information on quality control procedures are offered in the Supplementary Information (SI). Analysis methods are also briefly reported below:

- inorganic ions were determined by ionic chromatography after filter aqueous extraction in an ultrasonic bath.
- The Thermal Optical Transmittance (TOT) technique, by the Sunset Carbon Analyzer Instrument, was used to determine elemental carbon (EC) and organic carbon (OC) mass