



Seasonal changes, identification and source apportionment of PAH in PM_{1.0}



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HIGHLIGHTS

- Quantification of concentrations of PAHs in PM_{1.0}.
- Mean PAHs and PM_{1.0} concentrations were higher in winter, particularly HMW.
- Diagnostic ratios and PMF analysis confirmed influence of vehicular emissions.
- Correlation of PAHs with meteorological parameters.
- BaP and DahA dominated BaPeq levels in the study area, varying with the season.

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ABSTRACT

The objective of this research was to evaluate the seasonal variation of PAHs in PM_{1.0}, as well as to identify and quantify the contributions of each source profile using the PMF receptor model. PM_{1.0} samples were collected on PTFE filters from August 2011 to July 2013 in the Metropolitan Area of Porto Alegre, Rio Grande do Sul, Brazil. The samples were extracted using the EPA method TO-13A and 16 Polycyclic Aromatic Hydrocarbons (PAHs) were analyzed using a gaseous chromatograph coupled with a mass spectrometer (GC–MS). Also, the data discussed in this study were analyzed to identify the relations of the PAHs concentrations with NO_x, NO, O₃ and meteorological parameters (temperature, solar radiation, wind speed, relative humidity). The results showed that in winter, concentrations of total PAHs were significantly higher than in summer, thus showing their seasonal variation. The identification of emission sources by applying diagnostic ratios confirmed that PAHs in the study area originate from mobile sources, especially, from diesel and gasoline emissions. The analysis by PMF receptor model showed the contribution of these two main sources of emissions, too, followed by coal combustion, incomplete combustion/unburned petroleum and wood combustion. The toxic equivalent factors were calculated to characterize the risk of cancer from PAH exposure to PM_{1.0} samples, and BaP and DahA dominated BaPeq levels.

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1. Introduction

Polycyclic aromatic hydrocarbons (PAHs), also known as polynuclear aromatic hydrocarbons or polyarenes, constitute a large class of organic compounds (Dabestani and Ivanov, 1999). The PAHs

released into the atmosphere are normally present in the gaseous phase or sorbed to particulates. Low Molecular Weight (LMW) PAHs have a higher concentration in the gas phase, whereas High Molecular Weight (HMW) PAHs are often associated with atmospheric particulate matter (Bi et al., 2003). HMW PAHs are expected to require much longer time to partition to coarse particles than LMW PAHs (Duan et al., 2007).

PAHs are generated from the incomplete combustion or pyrolysis of organic material (Li et al., 2005). Amongst the PAHs sources are: combustion processes: coal and wood burning, oil and gas burning, vehicles engines and open burning. Mobile sources or

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open/uncontrolled burning, together with domestic combustion processes, are likely to provide the majority of the human exposure to atmospheric PAH, since humans congregate in urban environments characterized by these sources (Howson and Jones, 2010). Zhang and Tao (2009) showed, also, that the major anthropogenic atmospheric emission sources of PAHs include biomass burning, coal and petroleum combustion, and coke and metal production.

Atmospheric particles <1 μm are formed by primary particles resulting from combustion (Zhao et al., 2008; Wingfors et al., 2011). This particle size fraction consists of nucleation mode (from particles combustion engine vehicles) and accumulation mode (photochemical smog particles and combustion) (Bathmanabhan and Madanayak, 2010). In urban environments, the atmospheric particles emitted by mobile sources, over 90% of the number concentration, belongs to the fraction <1 μm (Bond, 2004; Morawska et al., 2008). This fraction can affect health and, in the other hand, can be a good indicator of vehicular sources in roadside sites (Lee et al., 2006). Given that, becomes important to study the PM_{1.0} particles in heavy traffic areas.

PAHs are ubiquitous in urban air and are a major health concern, mainly because of its known carcinogenic and mutagenic properties (Panther et al., 1999). The known carcinogens isomers are primarily associated with particulate material and, usually, the highest concentrations are in the respirable fraction <5 μm (Sierra et al., 2005). The PM_{1.0} particles present a higher risk because they can deposit in the respiratory tract, increasing the negative health effects (Slezakova et al., 2007) and can carry pollutants such as PAHs. Thus, there is considerable concern about the relationship between PAH exposure in the ambient air and the potential to contribute to human cancer incidence (Dybing et al., 2013). Nowadays, existing ambient air quality standards are restricted to PM_{2.5} and PM₁₀ fractions generated by mechanical processes and they are unable to effectively control submicron particles emitted from combustion sources such as motor vehicles (Morawska et al., 2008).

The emission sources identification of total PAHs concentration in ambient air can be accomplished through the use of diagnostic ratios or receptor models. The use of diagnostic ratios for PAH source identification involves comparing ratios of pairs of frequently found PAH emissions (Ravindra et al., 2008), however should be use with caution because the PAHs concentrations of emission sources can change due to the reactivity of PAHs with atmospheric species (ozone, nitrogen oxides) and environmental variables. In the present study, we used the positive matrix factorization method (PMF) because is considered a reliable receptor modeling, a powerful and widely used multivariate method that can resolve the dominant positive factors without prior knowledge of sources (Paatero and Tapper, 1994; Gu et al., 2011). In the work of Teixeira et al. (2013), the PMF model was used for apportionment of total PAHs in PM_{2.5} and PM₁₀ samples source.

Studies conducted in various locations around the world showed that the main sources of PAHs in urban areas are vehicular emissions, especially intense traffic and diesel vehicles, among which we cite some authors: Tsapakis et al. (2002), Guo et al. (2003), Manoli et al. (2004), Fang et al. (2004), Ravindra et al. (2006), Stroher et al. (2007). In Brazil, the analysis of the profile of PAHs concentrations was performed with particles of <10 and <2.5 μm , among which we mention: Barra et al. (2007), Bourotte et al. (2005), Dallarosa et al. (2005a, 2005b, 2008), De Martinis et al. (2002), Fernandes et al. (2002), Netto et al. (2002), Teixeira et al. (2012, 2013), Vasconcellos et al. (2011). However, studies of atmospheric particles <1 μm are scarce: Krupal et al. (2013), Klejnowski et al. (2010), Ladjji et al. (2009), among others.

Atmospheric particles in the fraction <1 μm bear a large surface area for adsorption of PAHs, therefore the fine and ultrafine particles are richer in PAHs than coarse ones (Da Limu et al., 2013; Fang

et al., 2006). Thus, the study of the concentration and behavior of PAHs in the fraction <1 μm is important to subsidize the knowledge of the probably negative impact on human health.

Consequently, ambient PM_{1.0} samples were collected during two years for PAH quantification in the study area. The objectives of this study were (i) to evaluate the seasonality of PAHs associated with airborne particulate matter <1 μm (PM_{1.0}), (ii) identify and quantify the contributions of each source profile using the PMF receptor model.

2. Experimental

2.1. Study area

The region is the most urbanized area of the state, is characterized by different types of industries, including some stationary sources such as the Alberto Pasqualini Refinery, steel mills – which do not uses coke- (Siderúrgica Riograndense e Aços Finos Piratini), III Petrochemical Industrial Complex, and coal-fired power plants (Termelétrica de Charqueadas e TERMOCHAR, and the Usina Termelétrica of São Jerônimo and the USTJ). Besides, it is estimated that the most significant contribution are mobile sources due to the large number of vehicles in circulation in the region (Teixeira et al., 2008, 2010; Agudelo-Castaneda et al., 2014). In the study by Teixeira et al. (2008) were found that of the total fleet in the study area, about 84.98% is fueled by gasoline, 6.67% diesel, 6.58% alcohol, 1.3% natural gas and 0.74% with flex technology. Currently, gasoline- fueled vehicles use a mixture of gasoline and 20% of ethanol (PETROBRAS, 2012). The diesel used in the Metropolitan Region of Porto Alegre (MAPA) has a level of 500 ppm of sulfur and it is added 5% of biodiesel (Mattiuzi et al., 2012). Even if the diesel fleet in the region is only 6.67%, the environmental impact caused by this source in the air is elevated. A study by Teixeira et al. (2012) shows that from the total emissions originating from mobile sources within the MAPA, diesel vehicles are responsible for most emissions of particulate matter and NO_x.

The sampling sites location (Sapucaia do Sul and Canoas) in the MAPA is shown in Fig. 1. The locations were selected due to their vehicular influence, although there are some differences between the two sites. Sapucaia do Sul site has a greater vehicular influence vehicle: light and heavy fleet, traffic congestions and slow speeds. This site also has low industrial influence (oil refinery, steel mills that do not use coke) upstream of prevailing winds. Canoas is under a strong vehicular influence, daily traffic congestions, Canoas air base and industries (oil refinery) upstream of the prevailing winds that have a medium influence in this sampling site.

The meteorological conditions were described in previous works (Teixeira et al., 2012), consequently here we are just including a brief explanation. Due to its location, the area of study presents well-defined seasons and a climate strongly influenced by cold air masses migrating from the polar regions. The study area is located in a subtropical, temperate climate with four well-defined seasons: summer (January–March), autumn (April–June), winter (July–September) and spring (October–December). The wind direction shows marked seasonal variations. During summer and spring, the prevailing direction is E–SE, while in fall and winter, besides E–SE winds, winds from W and NW also occur. The historical mean precipitation is 1.300–1.400 mm year⁻¹ (INPE-CPTEC, 2012). The weather conditions in the study area during the sampling period (August 2011–July 2013) were : average temperature 18.79 °C, ranging between –1.40 and 37.20 °C, mean relative humidity 79.92%, ranging between 16.80 and 100.00%, and mean solar radiation 224.18 W m². The maximum wind speed was 8.33 m s⁻¹ and the mean wind speed was 2.03 m s⁻¹, with resultant wind direction vector southeast (113°).

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