Atmospheric Research 101 (2011) 631–639

Contents lists available at ScienceDirect

Atmospheric Research

journal homepage: www.elsevier.com/locate/atmos

Study of nitro-polycyclic aromatic hydrocarbons in fine and coarse atmospheric particles

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ARTICLE INFO

Article history:
Received 30 November 2010
Received in revised form 15 April 2011
Accepted 19 April 2011

Keywords:
NPAHs
PAHs
CG/ECD
Mobile sources
Traffic
Diesel

ABSTRACT

The purpose of the present study was to evaluate six nitro-polycyclic aromatic hydrocarbons (NPAHs) in fine (<2.5 μm) and coarse (2.5–10 μm) atmospheric particles in an urban and industrial area located in the Metropolitan Area of Porto Alegre (MAPA), RS, Brazil. The method used was of NPAHs isolation and derivatization, and subsequent gas chromatography by electron capture detection (CG/ECD). Results revealed a higher concentration of NPAHs, especially 3-nitrofluoranthene and 1-nitropyrene, in fine particles in the sampling sites studied within the MAPA. The diagnostic ratios calculated for PAHs and NPAHs identified the influence of heavy traffic, mainly of diesel emissions. The correlation of NPAHs with other pollutants (NO_x, NO_2, NO and O_3) evidence the influence of vehicular emissions in the MAPA. The seasonal variation evidenced higher NPAHs concentrations in the fine particles during winter for most compounds studied.

1. Introduction

The atmosphere of urban centers contains various kinds of organic pollutants. Among them, there are several polycyclic aromatic hydrocarbons (PAHs) and nitro-polycyclic aromatic hydrocarbons (NPAHs), which are carcinogenic and/or mutagenic compounds (Tang et al., 2005).

The detection and characterization of PAHs and NPAHs in environmental samples is a priority, since both classes of compounds are ubiquitous. NPAHs are a group of organic compounds formed of two or more condensed benzene rings linked by a nitro group (NO_2). These compounds are widely distributed in the environment and are mainly found associated with atmospheric particles.

NPAHs present in the atmosphere originate from primary sources, such as emissions from mobile sources, mainly diesel vehicle exhaust (Nielsen, 1984; Bamford et al., 2003). In addition, NPAHs are also formed in the atmosphere via reaction of their parent PAHs initiated by hydroxyl (OH) radicals during the day and by nitrate (NO_3) radicals (in the presence of NO_x) during the night (Söderström et al., 2005; Atkinson and Arey, 1994) and/or the heterogeneous gas–particle interaction of the parent PAHs adsorbed onto particles with nitrating agents (Feilberg et al., 2001).

After being formed, and once released into the atmosphere, NPAHs are very persistent in the environment and can be carried over long distances from their original source (Nielsen, 1984; Ciccioli et al., 1996). To make matters worse, these compounds have 2.10^5 times the mutagenic and 10 times the carcinogenic potential compared to PAHs (Durant et al., 1996).

The temporal resolution of NPAHs in ambient air is limited by the detection limits of current analytical techniques. Collecting more samples or increasing the analytical sensitivity is required to increase the detectability of PAHs and NPAHs in ambient air (Crimmins and Baker, 2006). Because of the complexity of the matrices of environmental samples, the

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doi:10.1016/j.atmosres.2011.04.010

effectiveness of the methods depends critically on the "cleanness'' of the NPAH fraction achieved in the NPAH isolation step (Jinhui and Lee, 2001). In the environment, NPAHs are usually found at low concentrations (pg.g^{-1}–μg.g^{-1}) when compared to their parent PAHs (Feilberg et al., 2001); therefore, analysis techniques for detecting NPAHs must have high selectivity and sensitivity (Feilberg et al., 2001).

PAHs and NPAHs profiles measured by using a receptor resulted from the integration of several sources such as change in wind direction, oxidant concentration, and emission sources during the sampling period (Crimmins and Baker, 2006). These authors and others (Yamasaki et al., 1982; Mader and Pankow, 2000) reported that changes in temperature during a sampling period may alter PAHs and NPAHs profiles in the observed gas and particle distributions.

Most studies about NPAHs associated with atmospheric particles have been usually studies about NPAHs in fine atmospheric particles (e.g. Hayakawa et al., 1995; Kawanaka et al., 2004; Albinet et al., 2008; Di Filippo et al., 2010). These authors reported that most NPAHs were found in fine particles, revealing an important contribution of these compounds to mutagenicity.

In Brazil, few studies have been conducted about NPAHs in the atmosphere, among which we include those of the authors Vasconcellos et al. (2008), Barreto et al. (2007), and Pereira Netto et al. (2000).

The purpose of the present study is to identify and quantify the NPAHs associated with fine (<2.5 μm) and coarse (2.5–10 μm) atmospheric particles in an industrial/urban area (MAPA) heavily influenced by vehicle traffic, by applying the analytical method of gas chromatography by electron capture detection. The analysis of the influence of the major emission sources was done by diagnostic PAHs and NPAHs concentration ratios and by the correlation of NPAHs concentrations with other atmospheric pollutants such as O_3, NO, NO_2 and NO_x.

2. Area of study

The area chosen for this study was the metropolitan area of Porto Alegre (MAPA) located at 29°30′S – 30°30′S/50°25′W – 51°55′W in the east of the state of Rio Grande do Sul, Brazil. With a total area of 9800 km^2, it includes 31 counties and is the most urbanized area of Rio Grande do Sul.

The metropolitan area of Porto Alegre is characterized by different industrial typologies, including several stationary sources such as the Alberto Pasqualini oil refinery, two steel mills (Siderúrgica Riograndense and Aços Finos Piratini—which do not use coke) and two coal-fired power plants (Termochar and São Jerônimo). Despite the different industrial sources around Porto Alegre contributing to the total emissions, the major contributions come from an estimated 620,000 vehicles on local roads, representing 20% of the total 3.1 million vehicles of the state (Teixeira et al., 2008).

Due to the geographical location of the MAPA, the seasons are well defined and the rain is evenly distributed throughout the year. The historical rainfall average is 1300–1400 mm·year^{-1} (Livi, 1999). Winter in this region is strongly influenced by cold air masses migrating from polar regions, and in summer there is a greater influence of tropical, maritime and continental air masses.

According to Köppen's international climate classification system, the area of study has a climate described as Cfa subtropical climate with an average temperature above 22 °C during the warmest month of the year (Livi, 1999).

The prevailing wind directions are east (E), east southeast (ESE), and southeast (SE) (Livi, 1999). During the day, wind reaches its lowest speed at dawn and early morning, and highest speed in the late afternoon, between 5 and 7 p.m. This pattern is related to energy availability at the surface (sensible heat) during the day, intensifying local and mesoscale atmospheric circulations. The prevailing wind results from interactions of mesoscale phenomena, especially sea/land breezes (from the Atlantic Ocean and the Patos Lagoon) and valley/mountain breezes (from the nearby Serra Geral mountains to the north of the MAPA).

3. Methodology

3.1. Sampling

The sampling sites were located within the MAPA: Canoas, Sapucaia do Sul, and FIERGS (Porto Alegre), shown in Fig. 1. Samples of atmospheric particles were collected during a continuous period of 24 h every 15 days between 2006 and 2008 using a stacked-filter-units sampler (SFU) (Hopke et al., 1997), which separates fine and coarse particles: $PM_{2.5}$ and $PM_{2.5–10}$. The operational flow of the sampler (SFU) was 16.7 L.min^{-1} (Hopke et al., 1997). The particles were collected with quartz filters. The filters were equilibrated in a desiccator at room temperature for 24 h and weighed before and after sample collection. Each filter was wrapped in aluminum cover and stored at −20 °C until chemical analyses.

3.2. Extraction, cleanup and analysis

PAHs and NPAHs adsorbed onto the particulate matter (<2.5 μm and 2.5–10 μm) contained in the filters were extracted in Soxhlet with dichloromethane (CH_2Cl_2) for 18 h (USEPA, 1999). After this, extracts were separated/preconcentrated by cleanup procedure using silica gel column and three fractions of eluents of different polarities (ASTM, 2004, modified; Dallarosa et al., 2005a, 2005b, 2008).

The aliphatic compounds were eluted in the first fraction by using 20 mL n-hexane, which was then discarded. The PAHs were eluted in the second fraction, by using successively 20 mL of a mixture of n-hexane: dichloromethane (1:1) and 20 mL of the same solvents at 3:1 ratio. The volume of both elutions was collected in a single flask for subsequent volume reduction. The NPAHs were eluted in the third fraction by using 20 mL of dichloromethane, with the eluted volume being collected in a flask for subsequent volume reduction.

After isolation by cleanup, the derivatization of the third-fraction extracts was performed, in which NPAHS were fluorinated through specific chemical reactions with heptafluorobutyric anhydride (HFBA), according to the method proposed by Jinhui and Lee (2001). After that, NPAHs analysis 1-nitronaphthalene (1NNa), 2-nitrofluorene (2NNl), 3-nitrofluoranthene (3NFl), 1-nitropyrene (1-NPyr) and 6-nitrochrysene (6-NCry) was performed by gas chromatography/electron