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Study of the chemical elements and polycyclic aromatic hydrocarbons in atmospheric particles of PM_{10} and $PM_{2.5}$ in the urban and rural areas of South Brazil

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Abstract

The purpose of this work is to study the chemical elements and PAHs associated with atmospheric particulate in samples of PM_{10} collected in the Metropolitan Area of Porto Alegre—MAPA, Rio Grande do Sul, Brazil. In addition, to study the chemical elements associated with particles of different fractions of $PM_{10-2.5}$ and $PM_{2.5}$ using dichotomous sampling, in urban (MAPA) and rural areas. Two types of samplers were used: HV PM_{10} and Dichotomous ($PM_{10-2.5}$ and $PM_{2.5}$). Samples were collected during 2002 and 2005. The concentration of the elements Si, S, Cl, K, Ca, Ti, V, Cr, Mn, Fe, Ni, Cu, and Zn was determined by PIXE (Particle-Induced X-ray Emission), while the concentrations of 16 major PAHs were determined according to EPA with a gas chromatograph coupled to a mass spectrometer (GS/MS). Results showed that elements of anthropogenic origin (V, Zn, Cr, Ni, Cu, and S) were mainly associated with the fraction $PM_{2.5}$, while the soil dust (Si, Al, Ti and Fe) were found mainly on fraction $PM_{10-2.5}$. In samples of PM_{10}, the most frequent PAHs found were Bgp, Flt, BaA, Chr, B(b+k)F, BaP and Dba. The types of emission and their association with the atmospheric parameters were studied applying the statistical analysis of the principal component method. The main sources found in the area under study were vehicles, industries (steel mills and a coal-fired power station), dust, sea breeze, and burning.

Keywords: Metals; Polycyclic aromatic hydrocarbons; Atmospheric particles; Principal components analysis

1. Introduction

During the past decades, government efforts to control air pollution have achieved some positive effects, and, as a result, atmospheric pollutants have been reduced significantly. In many locations, evidence of the decline in pollutant concentrations has been reported (Azimi et al., 2003; Cortes et al., 2000). However, air pollution is still a

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major problem and tighter emission controls are being enforced by many governments.

Atmospheric particles have received special attention lately because control equipment used at industrial plants, coal-fired power stations, etc., are sometimes not controlling fine particles very effectively and, in addition, there are also the emissions of airborne particles from diesel and gasoline vehicles. Previous investigations (Lim et al., 2005) reported a direct association between particles and health effects. In particular, fine particles with sizes less than 2.5 μm ($PM_{2.5}$) have been targeted because of their potential health effects and their ability to be transported over long distances (Wilson and Spengler, 1996). Due to their large surface areas, such particles are also capable of carrying many chemical constituents.

The atmospheric particles comprise a complex mixture of different elements and compounds. These are, basically, constituted of sulfates, nitrates, ammonium, organic compounds (PAHs, nPAHs and others), marine salts (NaCl), soil elements (Al, Si, Ti, Ca, Fe), heavy metals (Pb, Zn, Ni, Cu, V, Cr, Cd, and others).

Metallic elements originate from different anthropogenic sources and are associated with different particles fractions. Those emitted during the burning of fossil fuels (V, Co, Mo, Pb Ni and Cr) (Pacyna, 1986; Lin et al., 2005) were mostly associated with particles smaller than $PM_{2.5}$. As, Cr, Cu, Mn and Zn are released into the atmosphere by metallurgical industries (Pacyna, 1986; Querol et al., 2002; Alastuey et al., 2006), and traffic pollution involves a wide range of trace element emissions that include Fe, Ba, Pb, Cu, Zn, and Cd (Pacyna, 1986; Birmili et al., 2006), which may be associated with the fine and coarse particles.

Anthropogenic sources of PAHs emission into the atmosphere include traffic, domestic heating, oil refining, and other industrial processes (Benner et al., 1989). PAHs occur both in gaseous form and adsorbed to particles in the atmosphere, depending on the volatility of the PAH species. Higher condensed molecules with four and more rings are particle-bound, whereas smaller PAHs mainly remain in the gas phase (Beak et al., 1991).

The major source of PAHs, particularly for large urban areas, is related to traffic and the number of gasoline and diesel vehicles (Kavouras et al., 1999; Samara et al., 2003; Kalaitzoglou et al., 2004). The highest concentrations of atmospheric PAHs are usually found in urban areas due to increasing vehicular traffic and scarce dispersion of atmospheric pollutants.

PAHs have attracted much attention in the studies on air pollution recently because some of them are highly carcinogenic or mutagenic. In particular, benzo [a]pyrene (BaP) has been identified as a highly carcinogenic compound (Park et al., 2002). Cd is suspected to interfere with the development of reproductive systems and Mn is the precursor for onset of neurological disorders at elevated exposure. Other elements like Ni cause allergic reactions while Pb is toxic, particularly to infants (Lim et al., 2005). Since inhalation is a major pathway of exposure to airborne chemical substances, information obtained on the chemical composition of urban air samples will assist in the assessment of possible human health risks.

Studies of the composition of urban air showed that polycyclic aromatic hydrocarbons (PAHs) contributed substantially to atmospheric pollution. Among these studies, we should mention Bourotte et al., 2005; Dallarosa, et al., 2005; Park, et al., 2002. Other studies of the elemental composition in atmospheric particles have also been conducted and used different techniques for the chemical assessment (Thomas and Morawska, 2002; Braga et al., 2004). However, there are few studies of the same area of PAHs and chemical elements associated with atmospheric particles. The present study will bring information on movable and fixed sources that are contributing to the contamination of organic and inorganic compounds in the atmosphere.

The purpose of this work is to study the chemical elements and PAHs associated with atmospheric particulate in samples of HV PM10 collected in the Metropolitan Area of Porto Alegre (MAPA), Rio Grande do Sul, Brazil. It will also study the chemical elements associated with particles of different fractions of $PM_{<10-2.5}$ and $PM_{<2.5}$ using dichotomous sampling, in urban (MAPA) and rural areas.

2. Study area

The Metropolitan Area of Porto Alegre (MAPA) is located in the mid-east area of Rio Grande do Sul, the southernmost state of Brazil (Fig. 1). It comprises 31 counties over 9825.61 km^2 and encompasses approximately 36% (3.7 million inhabitants) of the population of the state (IBGE, 2000). It is the major urban area of Rio Grande do Sul.

Due to its location, the MAPA climate is strongly influenced by cold air masses migrating from the polar region. Seasons are clearly defined and the rain is well distributed throughout the year. According to the Köppen climate classification system, the area under study is a Cfa type, that is, a humid subtropical climate with rains well distributed throughout the year and an average temperature above 22.0 °C during the hottest month of the year. The prevailing wind direction is SE, followed by the NE direction (EMBRAPA, 2003).