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Traffic and catalytic converter – Related atmospheric contamination in the metropolitan region of the city of Rio de Janeiro, Brazil

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Abstract

In this work, 24-h PM_{10} samples were collected in Rio de Janeiro, Brazil, and analysed for trace elements (Cd, Ce, Cu, La, Mo, Ni, Pb, Pd, Rh, Sb and Sn). The sampling was carried out at five locations (Bonsucesso; Centro, downtown city; Copacabana; Nova Iguaçu and Sumaré) with different traffic densities and anthropogenic activities. An analytical method based on the EPA method for the determination of trace elements in airborne particulate matter (PM), using ultrasonic-assisted extraction and inductively coupled plasma mass spectrometry (ICP-MS) was applied. Our results suggest that vehicular traffic is the most important source of environmental pollution at the studied sites. The presence of Mo, Pd and Rh in the analysed filters reflects an additional source of pollution caused by the erosion and deterioration of automotive catalytic converters.

Keywords: PM_{10}; Airborne particulate matter; Automotive catalytic converter; Trace elements

1. Introduction

Air pollution has been a major concern in modern urban and industrial areas (Park and Kim, 2005; Valavanidis et al., 2006; Srivastava and Jain, 2007). The problem concerning atmospheric contamination by airborne particulate matter (PM) has notably worsened in the last years due to the increase of motor vehicles, urban constructions, industries (Fernández et al., 2000) and waste incineration (Gómez et al., 2005). The release of these elements to the atmosphere can eventually affect the human health, since they can be deposited in lung tissues and other areas of the respiratory system during the breathing (Bilos et al., 2001; Yoo et al., 2002).

Elements such as Cd, Sb (Gómez et al., 2005), Pb (Gómez et al., 2001, 2005; Salma and Maenhaut, 2006), Cu (Gómez et al., 2001; Birmili et al., 2006), Ni (Park and Kim, 2005; Zotin et al., 2005), Sn (Viana et al., 2006), Ce (Morcelli et al., 2005), La (Gandhi et al., 2003), Mo (Baldanza et al., 2000; Gandhi et al., 2003),

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Pd, Pt and Rh (Baldanza et al., 2000; Gómez et al., 2001; Rauch et al., 2001; Lambrou et al., 2004; Morcelli et al., 2005; Bocca et al., 2006; Zotin et al., 2005) are traffic-related elements (TRE), which can be found in the atmosphere of the cities.

Cu (Birmili et al., 2006) and Sb (Gómez et al., 2005) are used as components in the brake pad material, and represent a public health concern, since the brake wear dust is partially inhalable (1–10 μm) (Birmili et al., 2006). Ni is associated to vehicular emissions, since it is used as a fuel additive (Park and Kim, 2005) and in automotive catalytic converters to minimize H_2S emissions (Zotin et al., 2005). Pb can be emitted to the atmosphere either from leaded-gasoline combustion (Zheng et al., 2004; Gómez et al., 2005), mechanical attrition (Salma and Maenhaut, 2006) or incineration of vehicle tires (Gieré et al., 2006). In 1989, Brazil was one of the first countries to remove Pb from automotive-gasoline.

The platinum-group elements (PGEs), primarily Pd, Pt and Rh are currently used in modern automotive catalytic converters for transformation of some pollutants, namely, C_xH_y, CO and NO_x, into less toxic substances (Gómez et al., 2001; Petrucci et al., 2004; Zereini et al., 2004; Morcelli et al., 2005; Bocca et al., 2006). Other elements such as Ce, La, Mo and Ni are also employed in the catalytic converter formulations (Gandhi et al., 2003; Baldanza et al., 2000; Morcelli et al., 2005; Zotin et al., 2005). In Brazil, catalytic converters based on Pd/Rh are used for gasoline vehicles (Morcelli et al., 2005), whereas Pd/Mo are used for alcohol vehicles (Baldanza et al., 2000).

In the State of Rio de Janeiro, PM_{10} glass-fiber filters are used by FEEMA, the environmental regulatory agency of the State, to monitor airborne particles up to 10 μm in aerodynamic diameter. High-volume samplers with glass fiber filters have been widely used for suspended PM collection in a number of contaminated areas because of their high collection efficiency for particulates and low flow resistance, even when they may contain relatively high levels of some trace elements as impurities (Smichowski et al., 2005).

Atmospheric concentration of trace metals in Brazil has been determined in some cities, such as Rio de Janeiro (Quiterio et al., 2004a,b), Niterói (Sella et al., 2004), Rio de Janeiro metropolitan area (Quiterio et al., 2005, 2006), Campinas (Miranda and Tomaz, 2007) and Salvador (Pereira et al., 2007). However, 24-h PM_{10} samples were collected only for Campinas and Salvador. Moreover, no report about atmospheric contamination by traffic-related elements (Ce, La, Pd, Rh and Sb) in Brazil was found.

This study presents the concentrations of trace elements collected on PM_{10} filters at five sites in the metropolitan area of City of Rio de Janeiro, Rio de Janeiro State, Brazil, from January to December 2005. Correlations between elements (Cd, Ce, Cu, La, Mo, Ni, Pb, Pd, Rh, Sb, Sn) and PM_{10} concentrations were determined by Pearson's correlation analysis. Clusters analysis was applied to the PM_{10} levels.

2. Experimental

2.1. Equipment

A sector field ICP-MS instrument (Element; Finnigan MAT), running in the low-resolution mode, was used for the elemental analysis. Indium at final concentration of 1 ng g^{-1} was used as internal standard. The extraction of the elements from the filters was performed by using a heated ultrasonic bath (Thornton) or a microwave oven (CEM Model Mars 5), a vortex mixer (FANEM Model 251) and a centrifuge (FANEM Model Excelsa 3 plus 280).

2.2. Reagents and standards

All reagents used were of the highest purity available or at least of analytical reagent grade. Water was distilled and deionized (Milli-Q, Millipore Corp., Millford, MA, USA), and nitric acid was purified by sub-boiling double distillation in a quartz apparatus. Ultra-pure HCl solution (Merck, Darmstadt, Germany) was used to prepare an acid mixture containing 5.55% w/w of HNO_3 and 16.75% w/w of HCl. All calibration solutions and the internal standard solution were daily prepared by diluting the 1000 mg l^{-1} stock solutions of the elements (Spex Industries Inc., Edison, NJ, USA). All intermediate solutions were stored in polyethylene bottles. Glassware was cleaned by soaking in 10% v/v HNO_3 for 24 h and rinsing at least three times with Milli-Q water. Then, the material was dried and stored in a class 100 laminar flow hood.

2.3. Sample collection

The climate of the metropolitan area of Rio de Janeiro City is Atlantic tropical with summer rains and warm summers. In 2005, there were about nine million inhabitants and two million registered vehicles. It experienced an average maximum temperature of 27.6 °C in March and an average minimum temperature of 22.0 °C in June. Annual average relative humidity was 73%. The rainfall varied in the range of 6 mm in August to 183 mm in December. Winds were predominantly southwest with monthly average speed varying in the range of 3.1–3.6 m s^{-1} (Meteorological National Institute of Brazil).

The sampling was conducted in five permanent sampling stations of FEEMA in the metropolitan area of Rio de Janeiro City (Fig. 1): Sumaré station (22° 55′ S and 43° 13′ W), considered as an altitude background site by FEEMA, is located in a sub-tropical forest, about 700 m above the sea level and close to a poor residential area (slum); Centro station (22° 54′ S and 43° 10′ W) is located in downtown Rio de Janeiro, on the margins of Guanabara Bay, with intensive car and bus traffic; Copacabana station (22° 57′ S and 43° 11′ W) is located inside an electrical substation, near Copacabana beach, and it is a residential and commercial area with intense car and bus traffic; Nova Iguaçu station (22° 45′ S and 43° 26′ W) is placed in an