

Urban air pollution: a representative survey of PM_{2.5} mass concentrations in six Brazilian cities

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Abstract In urban areas of Brazil, vehicle emissions are the principal source of fine particulate matter (PM_{2.5}). The World Health Organization air quality guidelines state that the annual mean concentration of PM_{2.5} should be below 10 µg m⁻³. In a collaboration of Brazilian institutions, coordinated by the University of São Paulo School of Medicine and conducted from June 2007 to August 2008, PM_{2.5} mass was monitored at sites with high traffic volumes in six Brazilian state capitals. We employed gravimetry to determine PM_{2.5} mass concentrations, reflectance to quantify black carbon concentrations, X-ray fluorescence to characterize elemental composition, and ion chromatography to determine the composition and concentrations of anions and cations. Mean PM_{2.5} concentrations and proportions of black carbon (BC) in the cities of São Paulo, Rio de Janeiro, Belo Horizonte, Curitiba, Recife, and Porto Alegre were 28.1±13.6 µg m⁻³ (38% BC), 17.2±11.2 µg m⁻³ (20% BC), 14.7±7.7 µg m⁻³ (31% BC), 14.4±9.5 µg m⁻³ (30% BC), 7.3±3.1 µg m⁻³ (26% BC), and 13.4±9.9 µg m⁻³ (26% BC), respectively. Sulfur and minerals (Al, Si, Ca, and Fe), derived from fuel combus-

tion and soil resuspension, respectively, were the principal elements of the PM_{2.5} mass. We discuss the long-term health effects for each metropolitan region in terms of excess mortality risk, which translates to greater health care expenditures. This information could prove useful to decision makers at local environmental agencies.

Keywords Fine particulate matter · Long-term health effects · Urban pollution · Aerosols · Brazil

Introduction

Brazil has a territory of 8.5 million square kilometers and a population of more than 160 million inhabitants, distributed throughout 26 states. The capitals of those states have been greatly affected by air pollution. In urban areas, the atmospheric particles that lead to health problems are common pollutants. This calls for exhaustive studies of mass concentrations and aerosol composition, because elevated concentrations of particulate matter (PM) have been associated with increased morbidity and mortality from cardiovascular and respiratory diseases (Saldiva et al. 1994; Lanki et al. 2006; Stolzel et al. 2007; Pope and Dockery 2006).

Aerosols are introduced into the atmosphere from a variety of anthropogenic sources, including transport, industrial activities, and biomass burning, as well as from natural sources, such as volcanic eruptions, sea salt, soil dust suspension, and forest fires. Urban pollution is generally composed of coarse and fine particulate matter from mineral dust, combustion processes, sulfur dioxide (SO₂), nitrogen oxides, ammonia, volatile organic compounds (VOCs), and carbon (black and organic). The SO₂, ammonia, and nitrogen oxides are precursors of the sulfuric

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acid, ammonium bisulfate, ammonium sulfate, and ammonium nitrate particles that often constitute major fractions of $PM_{2.5}$ and PM_{10} . Most particulate emissions from combustion sources are $PM_{2.5}$ mass fractions. Fine particles can be directly emitted by sources or produced by condensation, coagulation, or gas-to-particle conversion, the last being common to combustion sources. Detailed descriptions of atmospheric aerosols can be found in the literature (Seinfeld and Pandis 1998; Finlayson-Pitts and Pitts 2000).

Brazil is unique among countries in that it obtains 70% of its electricity from hydroelectric power plants and uses ethanol and gasohol on a broad scale for its light-duty vehicle fleet. Transportation is responsible for more than 60% of all petroleum consumption in Brazil (BEN 2009). In urban areas, heavy-duty diesel-powered vehicles are the main source of $PM_{2.5}$, the principal marker of which is black carbon (Sánchez-Ccoyllo et al. 2009).

The Brazilian National Ambient Air Quality Standard (NAAQS) sets the 24-h limit for coarse inhalable particulate matter ($PM_{2.5-10}$) at $150 \mu\text{g m}^{-3}$. However, for fine particles ($PM_{2.5}$) there is no NAAQS (CETESB 2009). It is noteworthy that $PM_{2.5}$ can penetrate more deeply into the human respiratory system than can $PM_{2.5-10}$, exacerbating diseases such as asthma and even inducing heart problems (Saldiva et al. 1994; Lanki et al. 2006; Stolzel et al. 2007). In most urban areas of Brazil, vehicles are considered the principal source of pollutants emitted into the atmosphere.

In Brazil, there are neither established networks nor any coordinated efforts for the evaluation of PM concentrations. The few data that are available were obtained primarily in isolated, short-term studies conducted in small areas. However, there have been some city-wide and regional studies. Orsini et al. (1986) conducted one of the first and most important multi-site studies in Brazil, evaluating the concentrations of particulate matter, between 1982 and 1985, at one natural forest seacoast site and in five urban-industrial cities (Vitória, Salvador, Porto Alegre, São Paulo, and Belo Horizonte). The authors showed that the annual NAAQS for PM_{10} ($50 \mu\text{g m}^{-3}$) was exceeded in the cities of Porto Alegre and São Paulo, whereas the mean $PM_{2.5}$ concentrations in Belo Horizonte, Porto Alegre, and São Paulo were 16.5, 14.3, and $29.0 \mu\text{g m}^{-3}$, respectively. Some authors have evaluated only PM_{10} concentrations, estimates of $PM_{2.5}$ concentrations being based on the knowledge that $PM_{2.5}$ typically accounts for 60% of the PM_{10} mass (WHO 2006).

The objective of the present study was to determine concentrations of particulate matter, in order to investigate differences between summer and winter concentrations, meteorological influences, physicochemical profiles, and the effects that $PM_{2.5}$ concentrations have on human health, in six major Brazilian cities (São Paulo, Rio de Janeiro, Belo Horizonte, Curitiba, Recife, and Porto Alegre), all of which are state capitals.

The Metropolitan Area of São Paulo (MASP) is the richest area in Brazil and is one of the largest megacities in the world, with more than 19 million inhabitants and 6 million vehicles, as well as a major industrial and technological park. Nevertheless, in recent decades, the economic situation has changed, and the economy of the MASP, which previously had a strong industrial profile, has become one that is focused on services and trades. The climate has been influenced by urbanization (Rodriguez et al. 2010). Air pollution, high building density, and a lack of green areas, combined with the proliferation of asphalt and concrete surfaces, have resulted in a greater number of urban heat island effects, fewer drizzle events, and rainfall events of greater intensity. The MASP has an extensive air quality monitoring network, which has shown that ozone levels often exceed the NAAQS limit during spring and summer, and that concentrations of inhalable particles exceed the NAAQS limit mainly during the winter, from June to August (CETESB 2009). In the winter and summer, the dry and wet seasons, respectively, temperatures range from moderate (average of 16°C in July) to high (average of 28°C in February). Table 1 presents geographic and climatic characteristics of the six Brazilian cities studied (Inmet-National Institute of Meteorology-www.inmet.gov.br). The historical average annual precipitation is 1,465 mm (Table 1), the rainiest months being December, January, and February (>300 mm/month). Studies of air pollution in the MASP have been carried out since the 1970s (Boueres and Orsini 1981; Orsini et al. 1986; Andrade et al. 1994). Such studies have focused on the characterization of inorganic $PM_{2.5}$ and PM_{10} . In the MASP, the reported concentrations of PM_{10} were once higher than were those of $PM_{2.5}$. However, this is no longer the case. The concentrations of PM_{10} can still be larger than those of $PM_{2.5}$, although the difference between both has become smaller than in the past. The concentrations of lead declined sharply after the introduction of ethanol (E95, 95% ethanol, 5% water) and gasohol (G80E20, 75% gasoline, 25% ethanol) as fuels. Although the concentration of SO_2 has decreased since the 1980s (Fornaro and Gutz 2006), the S particulate concentration has maintained approximately the same value ($1\text{--}2 \mu\text{g m}^{-3}$). Other, more recent, studies of particulate matter have been performed in the MASP (Castanho and Artaxo 2001; Miranda et al. 2002; Miranda and Andrade 2004). The results of those studies have demonstrated that aerosol concentrations are higher in the winter and that vehicle emissions constitute the main source of urban pollutants.

Rio de Janeiro is the second largest metropolis in Brazil and is one of the main economic, cultural, and financial centers in the country. It is also home to the two biggest Brazilian enterprises Petrobrás (a petrochemical company) and Vale (a mining and metallurgical concern). Historical average annual maximum and minimum temperatures are 27.2°C and 21.0°C , respectively (Table 1). July is the

Table 1 Geographic and climatic characteristics of the six Brazilian cities evaluated

Characteristic		São Paulo	Rio de Janeiro	Belo Horizonte	Porto Alegre	Curitiba	Recife
Coordinates	S	23.5	22.8	19.9	30.0	25.4	8.05
	W	46.7	43.2	43.9	51.2	49.2	34.9
Altitude (m)		800	Sea level	858	Sea level	934	Sea level
Annual precipitation (mm)		1,465	1,140	1,481	1,356	1,442	2,418
Annual temperature (°C)	Min.	15.6	21.0	16.6	15.6	12.5	21
	Max.	24.9	27.2	27.0	24.8	23.1	29
	Mean	19.3	25.0	21.1	19.5	16.9	25

Source: Instituto Nacional de Meteorologia (INMET, National Meteorology Institute)

coldest month and January is the hottest. Summer days are hot and humid, with temperatures above 40°C in isolated areas. In the winter, precipitation is rare and minimum temperatures are rarely below 10°C. Average annual precipitation is 1,140 mm, lower than for any of the other cities profiled here. Between 2003 and 2005, Godoy et al. (2009) studied PM₁₀ and PM_{2.5} concentrations at ten different sites in the city of Rio de Janeiro. The authors found that the concentrations of both were low, the lower and upper limits of PM_{2.5} concentrations being 7.3 and 11.4 µg m⁻³, respectively. At a site quite near that at which the samples analyzed in the present study were collected, the PM_{2.5} concentration was 11.1 µg m⁻³. In that study, anthropogenic sources, such as vehicle emissions and fuel combustion were found to have made a relatively high contribution to the fine aerosol mass, accounting for 52–75%.

The greater metropolitan area of Belo Horizonte is composed of 34 small cities, with 1.2 million vehicles, located in the mineral-rich region of the state of Minas Gerais, where there are great quantities of iron ore, manganese, gold, and calcareous rock. The region also features other important industries related to the metallurgical sector, such as companies dealing with non-metallic minerals (cement and lime), petrochemical concerns, and automobile manufacturers. In addition, trade, financial services, and public administration are crucial facets of the local economy. To the east, Belo Horizonte is flanked by the Serra do Curral Mountains (altitude, 1,390 m). Minimum and maximum monthly average temperatures are 16.6°C and 27.0°C, respectively, and the average annual precipitation is 1,480 mm (Table 1). In the greater metropolitan area of Belo Horizonte, where vehicle emissions constitute the main source of air pollution, there is a monitoring network for PM₁₀ and gases (www.feam.br). In 2006, the annual mean PM₁₀ concentration was 25.9 µg m⁻³ and was therefore (assuming again that PM_{2.5} accounts for 60% of PM₁₀) estimated to be 15.5 µg m⁻³ for PM_{2.5}.

Curitiba is located at a relatively high altitude (924 m) and has the lowest average annual temperature of any of the cities profiled here. Temperatures can drop to 5°C in winter and can rise to 30°C in summer. Annual average precipi-

ation is 1,442 mm (Table 1). Curitiba has one of the strongest economies in the southern region of Brazil, with industries in many sectors, such as food, furnishings, non-metallic minerals, wood, chemical/pharmaceutical products, and leather, which together account for more than 40% of the local gross domestic product (GDP). Despite having one of the best public transportation systems of Brazil, Curitiba has the lowest number of passengers per vehicle (Table 2), which can result in more vehicles circulating in the urban area. According to the most recent air quality report for Curitiba (www.meioambiente.pr.gov.br), PM₁₀ standards were not exceeded in the city in 2008. In the greater metropolitan area of Curitiba, there are only point events during which the air quality is poor.

The greater metropolitan area of Recife, in comparison with the other cities profiled here, has the lowest number of inhabitants, the smallest vehicle fleet, and the lowest GDP. Nevertheless, Recife is the most important medical and technology hub in the north of Brazil. Approximately 100 multinational companies, including Microsoft, Motorola, Borland, Inform Air, Oracle, Sun, and Nokia, have headquarters in the Recife area. It is considered the largest technology park in Brazil, in terms of revenue and number of companies. Tourism also plays an important role in the local economy. Emissions from ocean-going ships constitute a major source of particulate matter in the atmosphere over the area. The port of Recife handles an average of 2.2 million tons of cargo annually, and the main loads are sugar, wheat, corn, barley, malt, fertilizer, slag, and kelp (<http://www.portodorecife.pe.gov.br/doc/COMP-CARG.pdf>). Relative humidity is high throughout the year, and the annual average precipitation is 2,400 mm (Table 1). January is the hottest month, with temperatures above 30°C, whereas the lowest temperatures (≈20°C) are seen in July. To date, there has been no air pollution studies conducted in Recife. However, the city has air quality problems related to vehicle emissions, as well as to the emissions from ocean-going ships, which can pose a serious threat but have not been adequately addressed. The municipal public transport sector has adopted policies aimed at improving the quality of the vehicle fleet and the fuels employed.

Table 2 Population and vehicle fleet data of capital-cities and metropolitan areas (IBGE 2009 and 2008)

Characteristic	São Paulo	Rio de Janeiro	Belo Horizonte	Porto Alegre	Curitiba	Recife
Population (millions)						
City	11.0	6.18	2.45	1.44	1.85	1.56
GMA	19.4	11.1	5.01	4.10	3.42	3.26
GDP per capita (US\$×1,000)	14.7	11.5	7.9	11.8	10.5	6.8
Total vehicle fleet (millions)						
City	5.46	1.74	1.06	0.59	1.06	0.38
GMA	6.14	1.95	1.23	0.67	1.19	0.45
City vehicle fleet (million)						
Light-duty ^a	4.25	1.45	0.80	0.47	0.82	0.28
Motorcycle ^b	0.68	0.16	0.14	0.07	0.12	0.06
Heavy-duty ^c	0.53	0.13	0.12	0.05	0.12	0.04
Passengers/vehicle						
City	2.6	4.3	3.1	3.0	2.3	5.5
GMA	3.2	5.7	4.1	6.1	2.9	7.2

GMA greater metropolitan area

^a Burning ethanol or gasohol (25% ethanol+75% gasoline)

^b Burning gasohol

^c Burning diesel

The greater metropolitan area of Porto Alegre has more than 4 million inhabitants and 0.6 million vehicles. It is the richest city in the south of Brazil and is second only to the MASP in terms of agricultural production, industrial output, and GDP (Table 2). The Porto Alegre area features several major industries that emit atmospheric pollutants, including an oil refinery, two metallurgical plants, a petrochemical industrial complex, and two large coal-fired power plants. The area is located at sea level, and the climate is therefore strongly influenced by cold air masses migrating from Polar Regions. Temperatures are high in the summer and low in the winter, the monthly average maximum and minimum temperatures being 24.8°C and 15.6°C, respectively (Table 1). Although annual average precipitation is 1,356 mm, there is no dry or wet season in Porto Alegre, where the monthly average rainfall rate ranges from 80 to 137 mm. Studies of particulate matter was conducted from October 2001 to December 2002 in Porto Alegre (Braga et al. 2005; Dallarosa et al. 2008). At a sampling site near that chosen for the present study, only PM₁₀ concentrations were measured, and the annual mean was found to be 28 µg m⁻³. Again considering that PM_{2.5} accounts for 60% of the PM₁₀ mass, the annual mean PM_{2.5} concentration was estimated at 16.8 µg m⁻³. The authors showed that the main emission sources in the area were vehicle emissions and industrial activities, both of which are associated with the presence of S and of the metals Cu, Zn, Ni, V, and Cr.

The present study is the first to carry out long-term sampling of PM₁₀ and PM_{2.5} concentrations in multiple cities in Brazil.

Methodology

Study design

In a collaborative effort involving several Brazilian institutions and coordinated by the University of São Paulo School of Medicine, urban atmospheric aerosol PM_{2.5} were sampled over a period of more than 1 year (June 2007 to August 2008) in six large cities within Brazil. The samples were analyzed for mass concentration and trace element composition. We employed gravimetry to determine PM_{2.5} mass concentrations, optical reflectance to quantify black carbon concentrations, energy dispersive X-ray fluorescence (EDXRF) to characterize elemental composition, and ion chromatography to determine the composition and concentrations of anions and cations.

Sampling sites

As can be seen in Fig. 1, the sampling sites were located in six state capitals: São Paulo, Rio de Janeiro, Belo Horizonte, Curitiba, Recife, and Porto Alegre. The sites were within central regions of the metropolitan areas, where the traffic volumes were high and the traffic was composed mainly of light-duty (gasohol- and ethanol-powered) vehicles and heavy-duty (diesel-powered) buses. Table 1 shows the geographic information and climatological data for the sampling sites. Population, GDP, and vehicle fleet data for each of the cities and for their greater metropolitan areas are shown in Table 2.

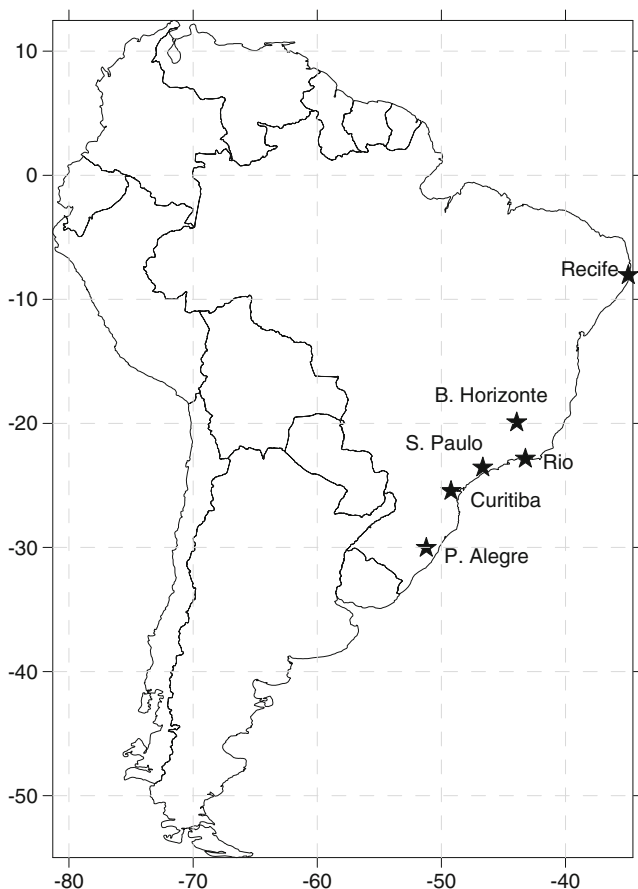


Fig. 1 Sampling area locations in Brazil and in South America

Sample collection

We collected 24-h particle samples using a PM_{2.5} Harvard Impactor, developed at the Harvard School of Public Health. The device was equipped with 37-mm polycarbonate filters (0.8 μm pore size) for PM_{2.5}. The sampler is composed of a vacuum pump with a system to monitor and regulate flow rate (10 L min⁻¹), a time counter and an impactor that allows only material with an aerodynamic diameter <2.5 μm to enter. The entire system was designed to provide the 50% cut-off point at 2.5 μm. Data regarding meteorological conditions (temperature, relative humidity, wind speed, and wind direction) were provided by the Brazilian National Meteorology Institute, in each case collected from the station that was closest to the sampling site. At each site, the local team was trained in order to guarantee good performance in the daily changing of filters, as well as in the cleaning and maintenance of the equipment.

Equipment and analyses

The polycarbonate filters were analyzed by gravimetry, optical reflectance, EDXRF, and ion chromatography, in

order to determine mass concentrations, black carbon mass, elemental composition, and ions, respectively.

The aerosol mass concentrations were obtained using an electronic microbalance with 1 μg readability (MX5; Mettler-Toledo, Columbus, OH, USA). Filters were stored in a temperature- and humidity-controlled environment (22±2°C and 45±3% relative humidity) for 24 h prior to weighing. Corresponding blank filters were analyzed, and the blank concentrations were subtracted from the values obtained for each sample.

Black carbon concentrations were determined by optical reflectance with a smoke stain reflectometer (model 43D; Diffusion Systems Ltd, London, UK). The calibration curve to convert from reflected light to black carbon concentration was obtained empirically using gravimetric standards. These calibration filters were prepared by ultrasonic nebulization (Clarke et al. 1987) with standard Monarch 71 carbon black (Cabot. Corp., Billerica, MA, USA), which was introduced by Heintzenberg (1982) as a reference material for light absorption measurements.

Elemental analysis was performed by EDXRF in a spectrometer (EDX 700HS; Shimadzu Corporation, Analytical Instruments Division, Tokyo, Japan). The sample is irradiated from below with X-rays. Detecting the energy condition of each element allows qualitative analysis, as well as quantitative analysis, because the fluorescence radiation is proportional to the quantity of the element. In the quantitative analysis, the system accurately computes the concentrations of the elements that can be determined via the signal intensities and/or over a suitable calibration curve obtained with standard reference material (Shimadzu Corporation). The background intensity of the X-ray tube (Rhodium anode) and the fluorescence radiation of the sample itself are used to correct changes in the absolute intensity of the signals, caused by the thickness or shape of the sample.

One-quarter of the filter was submitted to EDXRF, and spectra for fine fractions were accumulated for 900 s under the following conditions: Al filter, vacuum as X-ray path, 10-mm diameter collimator, 10–20 keV energy range, 50 kV tube voltage, an Rh X-ray tube, and a Si(Li) detector. We analyzed the elements Al, Si, P, S, Cl, K, Ca, Ti, V, Cr, Mn, Fe, Ni, Zn, Ga, Br, Zr, and Pb. The spectra were reduced with WinQXAS software, available from the website of the International Atomic Energy Agency (<http://www.iaea.org/OurWork/ST/NA/NAAL/pci/ins/xrf/pciXRFdown.php>).

For ion chromatography, 10 mL of ultra-pure water were added to the three-quarter filter fraction and extracted for 60 min in a mechanical shaking system. The solution was then filtered in a Millex polyvinylidene difluoride filter (0.22 μm pore size; Millipore, Bedford, MA, USA). The extract was kept frozen until analysis in a chromatograph with conductivity detection for major cations and anions (761 Compact IC; Metrohm, Herisau, Switzerland). Ana-

Table 3 Mean concentrations of PM_{2.5} and black carbon, together with the percentage contribution of BC, in the six Brazilian cities studied

City	<i>N</i>	PM _{2.5} (µg m ⁻³) Mean (SD)	BC (µg m ⁻³) Mean (SD)	%BC Mean (SD)
São Paulo	340	28.1 (13.6)	10.6 (6.4)	38 (14)
Rio	427	17.2 (11.2)	3.4 (2.5)	20 (7)
Belo Horizonte	371	14.7 (7.7)	4.5 (3.3)	31 (13)
Curitiba	320	14.4 (9.5)	4.4 (4.0)	30 (11)
Porto Alegre	342	13.4 (9.9)	3.9 (4.3)	26 (11)
Recife	327	7.3 (3.1)	1.9 (1.1)	26 (12)

N total number of samples

lytic conditions for anion determination were as follows: a 250×4 mm anion column (Metrosep A-Supp 5; Metrohm), eluent solution (4.0 mmol L⁻¹ Na₂CO₃/1.0 mmol L⁻¹ NaHCO₃), flow of 0.7 mL min⁻¹, a suppressor column (Metrohm), and regenerative solution (50 mmol L⁻¹ H₂SO₄). Analytic conditions for cation determination were as follows: a 150×4 mm cation column (Metrosep C2-150; Metrohm), eluent solution (4 mmol L⁻¹ tartaric acid/0.75 mmol L⁻¹ dipicolinic acid), flow of 1.0 mL min⁻¹, and an electronic suppression system (Metrohm). The analytical determination of each major ion was made using a calibration plot with a concentration range of 5–50 µmol L⁻¹.

Impact on mortality

To calculate the expected number of deaths attributable to air pollution, we modified the approach proposed by Ostro (2006), applying the following equation:

$$E = \beta \times D \times C / 10$$

where *E* is the expected number of premature deaths due to long-term exposure, *beta* is the percentage change in mortality per 10 µg m⁻³ change in annual concentration of PM_{2.5}, *D* is the number of natural deaths in the age group over 45 years of age, and *C* is the annual concentration of PM_{2.5} above the World Health Organization (WHO) annual air quality guideline (10 µg m⁻³).

Based on Ostro (2006), we assumed a *β* coefficient of 0.06, indicating that in a long-term exposure, an excess of 10 µg m⁻³ of PM_{2.5} is associated with a 6% increase in all-cause mortality in adults. Data on natural deaths in adults over 45 years were obtained from the Brazilian National Ministry of Health (Datusus et al. 2008) which currently uses the tenth revision of the International Classification of Diseases to categorize cause of death. Results are expressed as the percentage increase in the number of deaths as well as the number of deaths attributable to air pollution.

Results and discussion

Table 3 shows the number of samples collected during the study period, the mean PM_{2.5} concentrations, the mean

black carbon concentrations, and the proportion of PM_{2.5} represented by black carbon for each city and for the study period as a whole. The concentrations of PM_{2.5} were highest in São Paulo, which was followed by Rio de Janeiro, Belo Horizonte, Curitiba, Porto Alegre, and Recife. However, the same was not true for the concentrations of black carbon and its percentage contribution to PM_{2.5}. It is of note that the percentage contribution of black carbon was lowest in Rio de Janeiro, probably because diesel-powered (heavy-duty) vehicles represent a smaller proportion of the total vehicle fleet in Rio de Janeiro than in the other evaluated cities. Likewise, Curitiba and Belo Horizonte, which have similar proportions of heavy-duty vehicles in their fleets, showed comparable percentage contributions of black carbon (Table 2).

In Rio de Janeiro vehicles pollutant emissions inspection are taking place since 1997 (www.inea.rj.gov.br), while for São Paulo the inspection started in 2009 and it does not applied in the other cities. For a study performed in six European cities (Silanpaa et al. 2006), black carbon concentrations were all below 10% being the same for

Table 4 Concentrations of trace elements^a, in the summer and winter, in the ambient air of urban areas around the world

City/region	PM _{2.5} concentrations (µg m ⁻³)	
	Summer	Winter
São Paulo, Brazil (this study)	23.1	35.5
Rio de Janeiro, Brazil (this study)	15.8	23.0
Belo Horizonte, Brazil (this study)	14.5	18.5
Porto Alegre, Brazil (this study)	13.9	19.3
Curitiba, Brazil (this study)	13.3	18.1
Recife, Brazil (this study)	10.5	12.5
Beijing, China (Zhao et al. 2009)	85.8	91.1
Yokohama, Japan (Khan et al. 2010)	20.8	21.1
Agra, India (Kulshrestha et al. 2009)	64.2	144.2
Zonguldak, Turkey (Akyuz and Çabuk 2009)	32.4	83.3
United States ^a (Bell et al. 2007)	16.2	13.9
Helsinki, Finland (Sillanpaa et al. 2000)	12.1	10.2

^a Multi-city study

USA (Bell et al. 2007). But higher percentages were observed in Helsinki, with 14% of $PM_{2.5}$ being explained by the BC (Viidanoja et al. 2002) and 43% for Paris (Ruellan and Cachier 2001). Both studies were performed in urban areas. The high percentages found for the six Brazilian cities are not unusual in Brazil—previous studies found values around 30% of BC in the $PM_{2.5}$ (Castanho and Artaxo 2001; Miranda and Tomaz 2008; Godoy et al. 2009).

Because of the great number of samples, together with the variations in the concentrations related to the sources and to changes in meteorological conditions over the study period, the standard deviations were high.

For comparison purposes, Table 4 presents the $PM_{2.5}$ concentrations in the ambient air of urban areas in various cities and regions around the world (Zhao et al. 2009; Khan et al. 2010; Kulshrestha et al. 2009; Akyuz and Çabuk 2009; Bell et al. 2007; Sillanpaa et al. 2000). In the

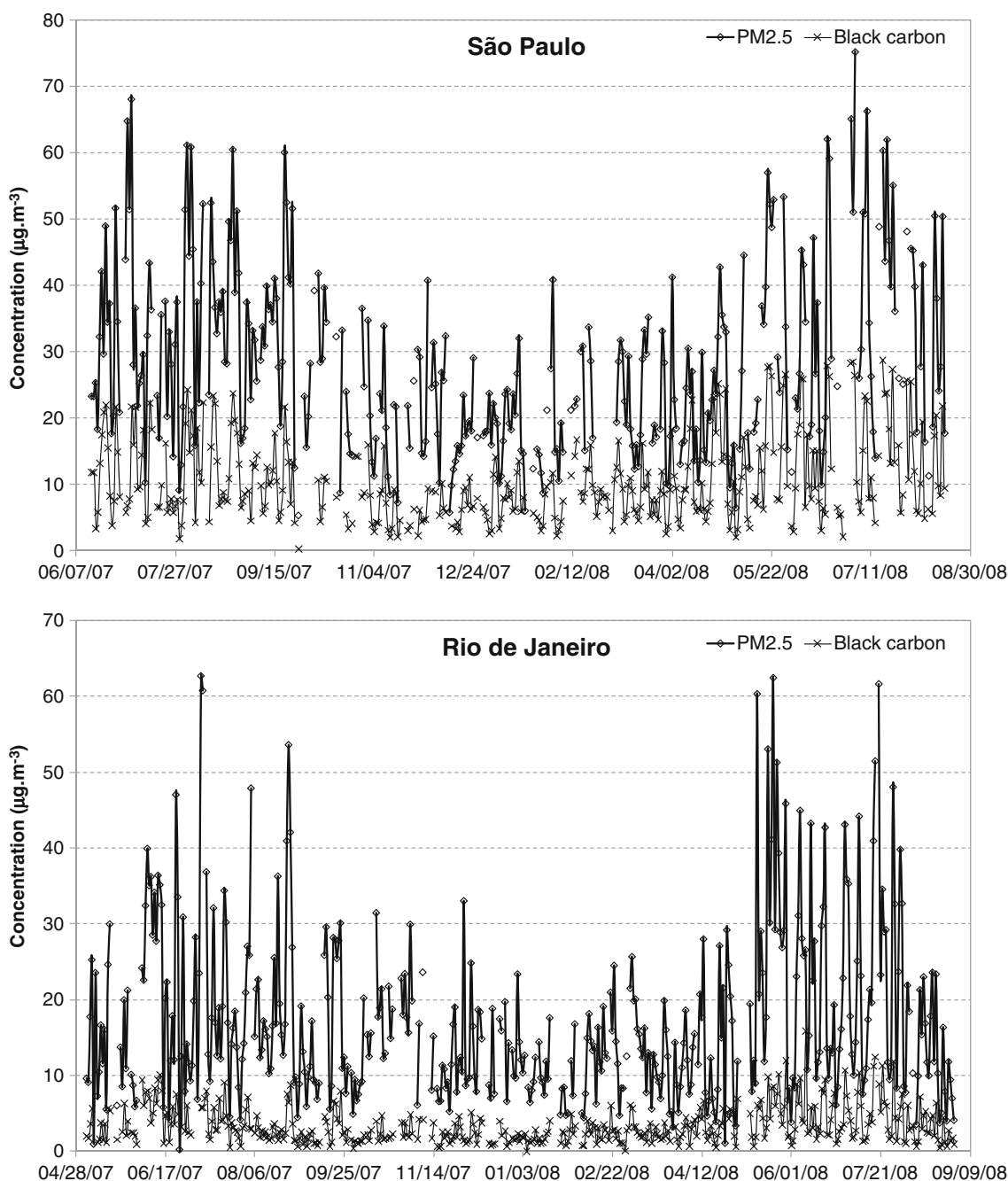


Fig. 2 Seasonal distribution for $PM_{2.5}$ and black carbon in micrograms per cubic meter for São Paulo, Rio de Janeiro, Belo Horizonte, Curitiba, Porto Alegre, and Recife

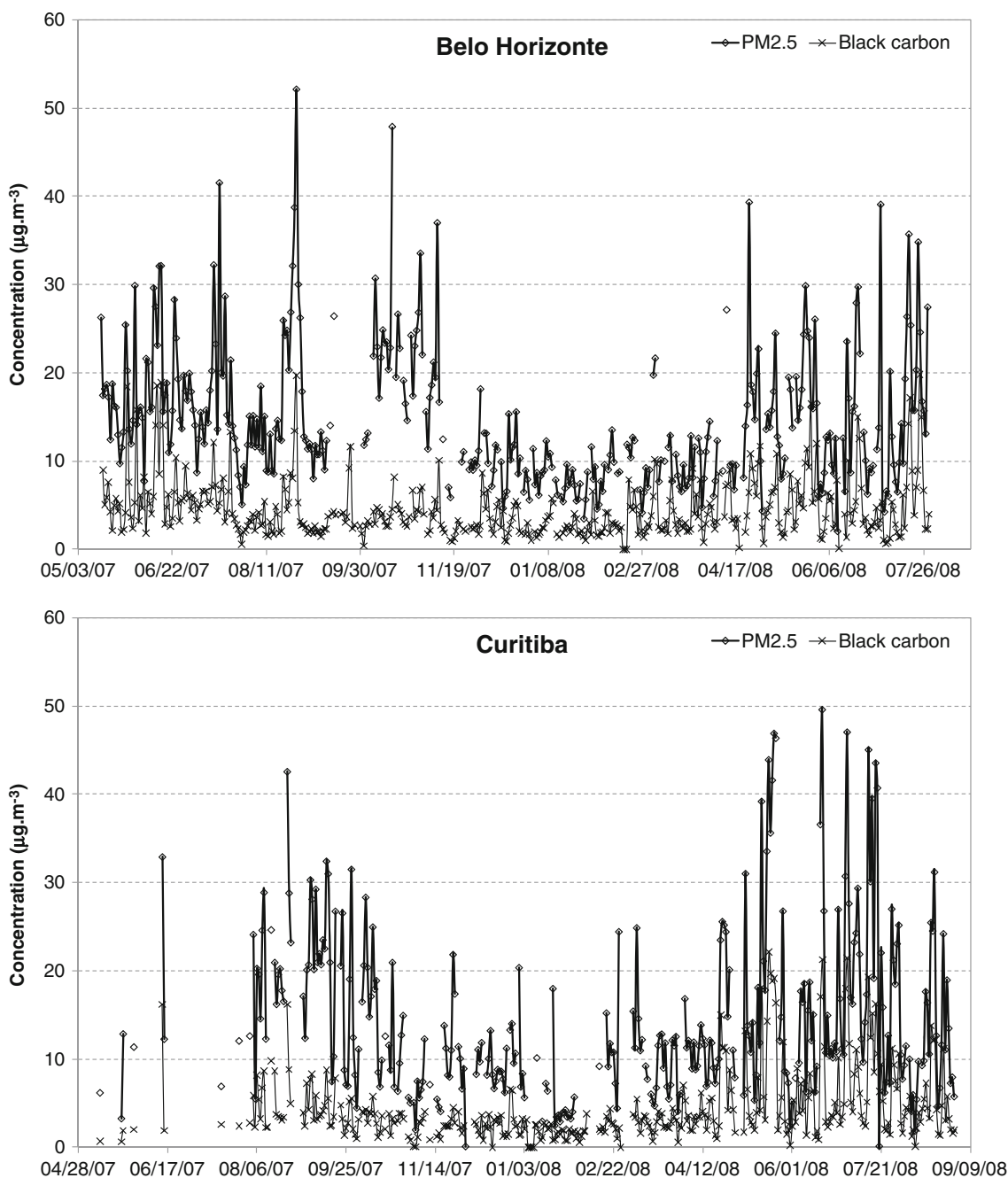


Fig. 2 (continued)

Brazilian cities studied here, $PM_{2.5}$ concentrations were generally lower than those reported for other major cities, in terms of the annual average values.

Seasonal variation

Figure 2 displays the seasonal variations in $PM_{2.5}$ and black carbon concentrations for all six cities evaluated. In general, concentrations were lower in the summer months (November to February), the exception being

Recife, where concentrations remained low throughout most of the year. It is difficult to compare concentrations among cities because there are numerous variables, such as the total number of vehicles, the proportions of vehicles burning the various types of fuels (Table 2), and meteorological parameters (Table 1). Nevertheless, it is clear that concentrations of $PM_{2.5}$ and black carbon were highest in São Paulo (Table 3).

In some countries in the North Hemisphere, the differences between winter and summer PM concentrations are

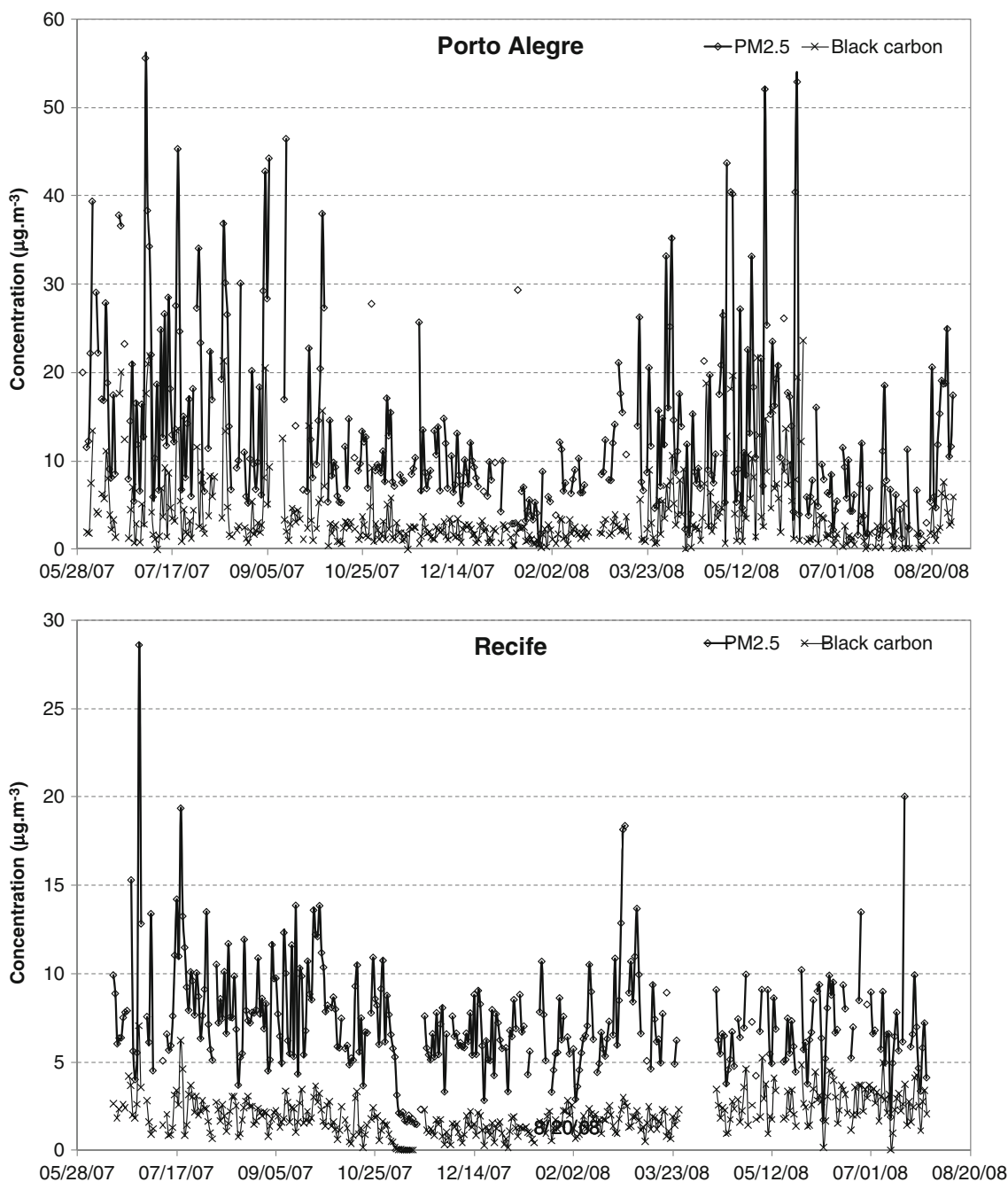


Fig. 2 (continued)

due to home heating, changes in the number of cars on the streets, and other seasonal characteristics (Akyuz and Çabuk 2009). It is of note that, in the cities evaluated in the present study, with the possible exception of Porto Alegre, there are no extreme seasonal variations in human behavior and activities. Therefore, although meteorological conditions (temperature, relative humidity, wind speed, and wind direction) seem to have influenced PM_{2.5} concentrations in the six capitals, other characteristics typically remained the same throughout the year and had no seasonal effects.

Meteorological conditions

Meteorological conditions had a great influence on PM_{2.5} concentrations. Table 5 presents 3-month averages for temperature, relative humidity, wind speed, PM_{2.5} concentrations, black carbon concentrations, and accumulated precipitation, as well as showing the number of measurements taken.

Although there was little variation in wind speed, there was considerable variation among the cities in terms of

Table 5 Three-month averages for temperature, relative humidity, wind speed, PM_{2.5}, and black carbon, together with 3-month accumulated precipitation values

City (period) ^a	Temperature (°C)	Relative humidity (%)	Wind speed (m s ⁻¹)	<i>N</i>	Accum. prec. (mm)	PM _{2.5} (μg m ⁻³)	<i>N</i>	BC (μg m ⁻³)	<i>N</i>
SP (Jun–Aug)	17.5 (3.1)	67 (12)	2.0 (0.6)	81	150.4	34.3 (13.8)	71	12.2 (6.4)	71
SP (Sept–Nov)	20.3 (2.7)	70 (10)	2.3 (0.7)	91	331.0	27.1 (11.5)	66	8.1 (4.6)	62
SP (Dec–Feb)	21.9 (2.3)	74 (9)	2.2 (0.5)	91	750.6	19.9 (7.5)	67	7.8 (3.3)	71
SP (Mar–May)	19.9 (2.8)	71 (10)	2.1 (0.6)	92	342.4	24.7 (11.5)	78	10.8 (6.5)	88
SP (Jun–Aug)	17.5 (2.5)	69 (12)	1.8 (0.7)	91	146.2	35.7 (16.4)	58	13.8 (8.1)	67
RJ (Jun–Aug)	21.2 (2.4)	78 (10)	2.3 (0.7)	92	41.6	19.8 (12.4)	111	4.0 (2.5)	103
RJ (Sept–Nov)	23.5 (2.2)	78 (10)	2.4 (0.7)	88	272.2	14.7 (4.2)	72	2.4 (1.5)	72
RJ (Dec–Feb)	25.4 (2.4)	83 (10)	2.1 (0.6)	91	560.8	12.4 (5.5)	71	2.1 (1.2)	76
RJ (Mar–May)	23.5 (2.6)	85 (8)	1.9 (0.6)	91	364.2	17.3 (12.7)	84	3.6 (2.3)	83
RJ (Jun–Aug)	21.1 (2.3)	80 (10)	2.0 (0.8)	92	139.2	19.9 (12.6)	89	4.4 (3.2)	91
BH (Jun–Aug)	19.4 (1.8)	55 (8)	2.6 (0.8)	92	5.6	17.7 (7.7)	109	5.7 (3.9)	109
BH (Sept–Nov)	22.4 (2.3)	54 (11)	3.1 (0.9)	88	247.6	17.6 (8.0)	58	3.5 (2.0)	77
BH (Dec–Feb)	22.5 (1.7)	67 (11)	2.4 (0.8)	91	800.4	9.0 (2.8)	75	2.9 (1.7)	87
BH (Mar–May)	21.5 (1.7)	64 (9)	2.0 (0.7)	92	312.2	13.7 (6.6)	75	5.1 (3.2)	88
BH (Jun–Aug)	NA	NA	NA	NA	NA	14.8 (8.5)	54	5.1 (4.4)	56
CUR (Jun–Aug)	14.6 (3.6)	72 (10)	2.4 (0.6)	76	9.6	18.1 (9.0)	27	5.0 (4.1)	28
CUR (Sept–Nov)	18.3 (2.6)	75 (8)	2.6 (0.7)	88	351.2	14.5 (8.0)	75	3.3 (1.8)	75
CUR (Dec–Feb)	20.3 (2.1)	78 (6)	2.4 (0.6)	91	549.8	8.3 (4.7)	51	2.1 (1.2)	77
CUR (Mar–May)	17.4 (3.3)	78 (9)	2.0 (0.8)	71	380.8	14.5 (10.1)	80	5.2 (4.9)	85
CUR (Jun–Aug)	15.0 (2.9)	75 (11)	1.9 (0.8)	92	297.2	16.7 (10.7)	87	6.2 (4.8)	92
PA (Jun–Aug)	13.5 (3.8)	79 (11)	1.6 (0.7)	92	568.6	18.3 (10.7)	78	5.7 (5.4)	76
PA (Sept–Nov)	19.9 (2.8)	74 (10)	1.8 (0.7)	89	325.2	13.8 (9.8)	62	3.4 (3.5)	78
PA (Dec–Feb)	24.0 (2.0)	70 (8)	1.8 (0.5)	89	258.4	8.0 (4.2)	60	1.8 (0.8)	82
PA (Mar–May)	20.0 (4.2)	74 (8)	1.4 (0.6)	92	427.6	15.7 (10.2)	74	5.2 (4.7)	83
PA (Jun–Aug)	14.8 (3.0)	80 (9)	1.4 (0.7)	92	393.2	9.5 (9.0)	68	3.4 (4.2)	76
RE (Jun–Aug)	23.8 (0.7)	81 (4)	NA	81	832.0	8.7 (3.7)	69	2.4 (1.1)	67
RE (Sept–Nov)	25.2 (1.1)	72 (5)	2.8 (0.4)	91	185.0	6.9 (3.1)	86	1.5 (0.9)	84
RE (Dec–Feb)	26.7 (0.7)	71 (4)	2.6 (0.4)	91	148.6	6.8 (2.6)	75	1.4 (0.6)	89
RE (Mar–May)	25.4 (1.2)	82 (6)	1.6 (0.4)	85	1,029.8	6.9 (2.1)	53	2.1 (1.0)	65
RE (Jun–Aug)	NA	NA	NA	NA	NA	7.2 (2.9)	44	2.8 (1.0)	58

N total number of measurements, *Accum. prec.* accumulated precipitation, *SP* São Paulo, *RJ* Rio de Janeiro, *BH* Belo Horizonte, *CUR* Curitiba, *PA* Porto Alegre, *RE* Recife

^a Data collected from June 2007 to August 2008

Table 6 Average concentrations of anions and cations in the six Brazilian cities evaluated

Ion	Concentration (μg m ⁻³)					
	São Paulo Mean (SD)	Rio de Janeiro Mean (SD)	Belo Horizonte Mean (SD)	Porto Alegre Mean (SD)	Curitiba Mean (SD)	Recife Mean (SD)
Cl ⁻	0.24 (0.29)	0.11 (0.25)	0.04 (0.03)	0.15 (0.17)	0.07 (0.15)	0.15 (0.16)
NO ₃ ⁻	1.22 (1.09)	0.56 (0.80)	0.19 (0.13)	0.43 (0.43)	0.16 (0.13)	0.11 (0.06)
SO ₄ ²⁻	3.09 (1.98)	1.91 (1.41)	1.15 (0.51)	1.17 (0.91)	1.08 (0.68)	0.61 (0.33)
Na ⁺	0.24 (0.16)	0.21 (0.11)	0.08 (0.04)	0.19 (0.11)	0.10 (0.05)	0.33 (0.14)
NH ₄ ⁺	1.25 (0.89)	0.80 (0.78)	0.34 (0.19)	0.35 (0.36)	0.37 (0.27)	0.18 (0.13)

temperature, relative humidity, and accumulated precipitation. In São Paulo, Rio de Janeiro, Belo Horizonte, and Curitiba, the winter is characterized by lower temperatures, lower relative humidity, and less precipitation, resulting in higher concentrations of PM_{2.5} and black carbon. As expected, we observed a strong negative correlation between PM_{2.5} concentrations and accumulated precipitation. Precipitation can remove particles by rainout (in-cloud removal) and washout (below-cloud removal), as well as preventing the resuspension of soil dust (Seinfeld and Pandis 1998), thereby decreasing PM concentrations. In Porto Alegre and Recife, the situation is somewhat different. In Porto Alegre, precipitation is evenly distributed throughout the year, with only a slight increase during the winter months (June to September), concentrations of PM_{2.5} and black carbon being lower between October and February, when there is slightly less precipitation. In Recife, precipitation is heavy from March until July, and there is little variation in PM_{2.5} concentrations over the course of the year.

In São Paulo, relative humidity is lower in the winter months, as are wind speed and precipitation, winter being the dry season. Winter thermal inversions create conditions than can elevate pollutant concentrations, and winter conditions in general promote higher PM_{2.5} concentrations. The great number of tall buildings, combined with the proliferation of asphalt and concrete surfaces, can create urban heat island effects, which can also influence pollutant concentrations and other environmental conditions. In the summer months, concentrations are lower, because of the great number of low pressure systems, which favor pollutant dispersion.

We had expected to find a negative correlation between wind speed and PM_{2.5} concentrations, higher wind speeds resulting lower concentrations. However, we observed no such correlation for any of the six cities evaluated. Other authors have stated that this correlation is dependent on local sources and particle size (Khan et al. 2010; Tai et al. 2010).

Ion composition

The concentrations of major ions in PM_{2.5} are shown in Table 6. As expected, the concentrations of all ions were highest in São Paulo. In particular, we observed high concentrations of ammonium, which can be associated with vehicle emissions (reduction reactions in three-way catalytic converters) and biogenic emissions (Fontenele et al. 2009). In all six cities, the concentrations of sulfate were higher than were those of any other ion. The lowest sodium concentrations were observed in Belo Horizonte and Curitiba, which are farther from the ocean than are the other metropolitan areas. Comparing the element S, as analyzed by EDXRF, with the S present in sulfate (SO₄²⁻),

as analyzed by ion chromatography, we observed that all S in PM_{2.5} was in sulfate form. As can be seen in Fig. 3, this correlation was significant ($R=0.9822$, angular coefficient=1.004 and linear coefficient=0.008).

Elemental composition

Table 7 presents the mean values obtained in the EDXRF analysis for the summer months (October to March) and winter months (April to September), as well as the total numbers of samples analyzed. As previously mentioned, concentrations were higher during the winter.

Soil-derived elements presented high concentrations, although anthropogenic elements also appeared. Vanadium is produced by the burning of diesel and oil, whereas S derives from combustion processes. The latter is present in sulfate form from SO₂ oxidation (Fig. 3). Gaseous SO₂ is a product of fossil fuel combustion (Seinfeld and Pandis 1998). Manganese can be related to industrial processes, whereas Fe and Zn, in the fine fraction, are associated with combustion processes (Castanho and Artaxo 2001; Geller et al. 2006). Cu and Zn are commonly added to engine oils for their antioxidant properties (Ferreira da Silva et al. 2010). Potassium has been associated with biomass burning (Kundu et al. 2010). In cities located in southern Brazil, such as Curitiba and Porto Alegre, concentrations of K can also be associated with wood burning for heat during the winter.

With the exceptions of Si, S, K, Fe, and Zn, all of the elements showed similar concentrations among the six cities. Belo Horizonte is situated in a mining region, and the prevailing winds are from the ESE (from the mines and toward the city), which could explain the high concentrations of Si, Ca, Mn, and Fe, those of S being attributed to

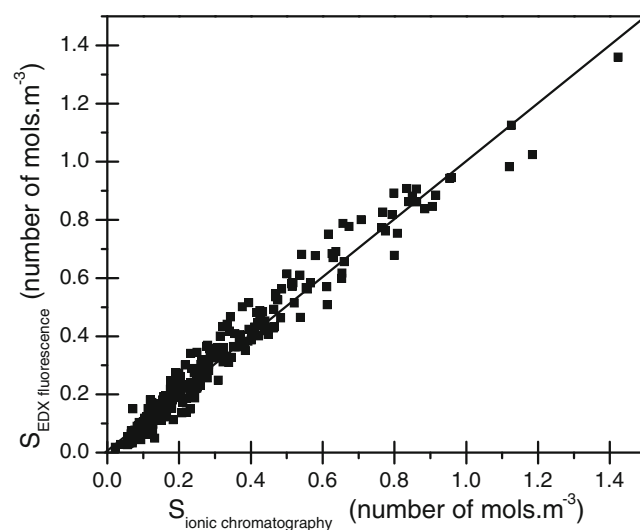


Fig. 3 Relation between sulfur (number of moles per cubic meter) measured by EDX analysis and sulfate by ionic chromatography

Table 7 Concentrations of PM_{2.5}, BC, and trace elements submitted to EDXRF analysis^a, for the summer months (October to March) and winter months (April to September)

Element	Sao Paulo (n=207) ^b			Rio de Janeiro (n=150) ^b			Belo Horizonte (n=217) ^b			Porto Alegre (n=174) ^b			Curitiba (n=155) ^b			Recife (n=148) ^b								
	Summer		Winter	Summer		Winter	Summer		Winter	Summer		Winter	Summer		Winter	Summer		Winter						
	Mean	SD	Mean	SD	Mean	SD	Mean	SD	Mean	SD	Mean	SD	Mean	SD	Mean	SD	Mean	SD						
PM _{2.5} ^c	23.1	9.5	35.5	14.5	15.8	5.5	23.0	13.0	14.5	6.5	18.5	7.5	13.9	6.7	19.3	14.3	13.3	5.1	18.1	9.2	10.5	2.8	12.5	4.6
BC ^c	7.1	3.4	13.1	7.3	2.3	1.2	4.0	2.5	3.4	1.7	5.8	4.4	2.6	2.4	4.9	5.0	2.7	1.4	5.0	4.1	1.3	0.6	2.7	1.1
Al	33.2	28.4	75.5	73.4	32.9	41.2	62.3	66.5	43.9	55.8	54.0	39.5	28.3	24.3	50.6	52.4	48.4	81.9	55.6	56.8	55.4	83.3	26.9	29.0
Si	76.6	49.9	196.7	149.1	77.9	63.0	153.3	153.7	162.4	126.5	223.5	133.6	74.8	60.6	86.0	111.7	74.3	74.4	101.8	103.8	139.7	163.8	58.5	39.5
P	36.4	147.9	24.3	17.6					9.5	48.6	4.5	4.0	7.1	8.2	12.0	43.8	5.4	5.2	4.8	5.1	1.9	1.5	3.1	3.5
S	896.6	472.0	967.1	544.8	638.2	398.8	672.9	485.3	331.5	195.0	388.9	181.6	389.0	348.4	339.0	295.5	384.0	260.3	390.5	263.7	228.6	104.5	165.5	107.8
Cl	33.5	49.5	161.2	202.4	18.8	54.6	91.6	142.8	11.1	34.8	10.0	15.9	54.5	80.5	114.3	193.5	41.8	189.9	24.3	55.7	58.8	64.6	176.8	177.7
K	137.6	130.1	363.5	221.0	124.9	281.0	241.4	187.7	141.2	140.4	224.9	131.7	158.5	156.7	322.3	320.2	154.6	151.4	356.5	289.4	117.4	77.7	158.9	193.2
Ca	52.7	26.6	119.5	108.8	31.9	23.7	53.7	62.8	98.5	72.5	96.2	52.8	35.8	22.5	38.3	40.6	37.0	35.0	49.3	53.3	53.5	29.9	53.7	40.5
Ti	5.7	3.2	13.1	10.5	4.4	3.5	6.5	5.4	4.4	4.1	5.4	3.2	3.7	2.7	5.2	6.0	4.0	3.8	5.1	4.9	4.0	5.2	2.2	1.0
V	1.3	0.9	2.0	1.5	4.9	2.9	3.8	2.2	1.5	0.8	1.6	0.8	0.9	0.5	1.5	1.0	0.7	0.6	0.7	0.9	0.4	0.3	0.3	0.2
Cr	1.0	1.0	2.1	1.8	1.8	0.7	1.8	0.7	0.7	0.9	0.6	0.6	1.3	0.7	12.1	69.1	0.7	0.6	0.8	0.8	0.4	0.4	0.5	0.5
Mn	6.6	21.2	8.2	5.0	3.7	1.9	5.0	3.4	25.2	60.5	49.2	44.9	2.8	2.8	6.2	19.7	2.1	4.4	2.5	2.2	1.3	1.3	2.9	3.4
Fe	128.3	57.2	247.9	142.6	56.3	26.4	89.5	65.9	107.9	80.6	142.6	77.7	60.2	44.9	90.7	134.3	57.3	31.7	82.9	59.9	50.7	46.7	74.4	52.4
Ni	0.9	1.5	1.2	1.1	3.6	1.5	2.2	1.4	0.8	0.5	0.8	0.6	0.7	0.2	4.7	13.9	0.4	0.5	0.9	0.8	0.3	0.3	0.4	0.5
Cu	8.1	13.8	13.1	9.8	7.7	4.8	9.9	10.7	4.1	6.4	2.5	3.8	1.9	1.8	5.2	7.5	2.6	4.2	3.8	4.8	0.9	0.9	1.8	1.8
Zn	53.6	41.1	99.0	96.1	18.1	15.9	30.9	26.5	12.6	12.3	16.1	13.5	12.4	18.9	18.7	20.2	9.0	10.6	25.8	46.1	8.9	10.9	24.9	28.9
Se	3.3	3.6	23.4	52.1					0.4	0.5	0.4	0.3	0.8	0.3	2.5	3.1	0.4	0.6	0.4	0.4	1.1	1.1	1.3	1.7
Br	2.8	2.7	7.8	9.4	4.5	2.1	7.8	4.9	2.5	1.8	2.4	1.6	2.4	1.3	3.4	2.6	2.0	1.5	3.5	3.3	2.9	1.5	3.5	3.1
Pb	15.4	12.6	22.4	20.5	9.5	7.1	14.1	11.4	3.0	4.8	6.7	8.1	3.2	3.1	5.4	5.4	7.9	15.8	11.5	16.2	2.1	1.9	4.5	4.6

^a Concentrations in nanograms per cubic meter, unless otherwise noted^b Number of samples for which elemental analysis data were available for the entire study period^c Concentrations in micrograms per cubic meter

Table 8 Concentration of PM_{2.5} in the ambient air of urban areas around the world

Element	This study ^a	Annual mean concentration (ng m ⁻³)			
		USA (nationwide) (Bell et al. 2007)	Atlanta, GA, USA (Liu et al. 2005)	Birmingham, AL, USA (Liu et al. 2005)	Hanoi, Vietnam (Cohen et al. 2010)
Al	43.9	29.2	22	21	224
Si	125.3	105	89	66	1,080
P	10.9	4.8			39
S	496.6	3,698 ^b			3,810
Cl	66.6	24.8			292
K	225.3	72.9	59	118	974
Ca	64.0	57	43	114	459
Ti	5.5	5.33			31
V	1.53	5.64			3
Cr	1.40	2.03			5
Mn	11.71	3.00	2	15	61
Fe	108.3	85.7	74	178	394
Ni	1.00	1.85			4
Cu	4.42	3.98	3	7	10
Zn	29.7	14	13	119	487
Se	3.45	1.62	1	1	
Br	3.75	3.14	4	5	15
Pb	8.39		5	26	236

^a Average for the six Brazilian cities evaluated

^b S in sulfate form

vehicle emissions. In Rio de Janeiro, the concentrations of S might also be related to the fact that there are oil refineries near the sampling site. However, wind direction analysis showed that the highest S concentrations were linked to wind coming not only from the direction of the refineries but also from urban areas. Therefore, S cannot be attributed to one source alone.

As can be seen in Table 5, the concentrations of K were highest in Curitiba, followed by Porto Alegre, São Paulo, Belo Horizonte, Rio de Janeiro, and Recife. However, it is likely that besides the biomass burning, biogenic sources can contribute to the concentrations of K, including materials such as pollen, spore, fragments of animals and plants, bacteria, algae, and fungi (Miranda et al. 2002).

São Paulo has the largest vehicle fleet and the highest vehicle emissions, which explains the high concentrations of S, Fe, and Zn. The average elemental compositions observed for all six Brazilian cities were higher than those reported for other cities in the US, for most of the elements (Table 8). On the other hand, concentrations were lower comparing to Hanoi in Vietnam (Cohen et al. 2010), in a sample area with intense sources due to coal thermoelectric power generation, but comparable to other studies around urban areas in Brazil (Dallarosa et al. 2008; Castanho and Artaxo 2001; Miranda and Tomaz 2008)

In a companion study (Andrade et al. 2010), principal component analysis was applied in order to evaluate the contribution of each source to the PM_{2.5} mass, with special

emphasis on the identification of the contribution made by vehicle emissions.

Table 9 shows, for each city, the annual mean PM_{2.5} concentration, the portion that exceeded the safe level recommended by the WHO, the annual mortality rate, and the estimated number of deaths associated with the excess PM_{2.5}. The annual mean PM_{2.5} concentrations exceeded the safe level in São Paulo, Rio de Janeiro, Belo Horizonte, Porto Alegre, and Curitiba, although not in Recife. São Paulo presented the worst results, in function of its larger population and higher PM_{2.5} concentrations, São Paulo

Table 9 Annual mean PM_{2.5} concentrations, PM_{2.5} concentrations in excess of the air quality guideline^a, annual mortality rate, and estimated number of deaths attributed to the excess PM_{2.5} concentrations, by metropolitan region

City	Annual mean PM _{2.5} (µg m ⁻³)	Excess (µg m ⁻³)	Annual mortality rate (%)	Excess mortality ^b (thousand)
São Paulo	28.1	18.1	11	9.7
Rio de Janeiro	17.2	7.2	4.3	2.7
Belo Horizonte	14.7	4.7	2.8	0.5
Porto Alegre	13.4	3.4	2.0	0.4
Curitiba	14.4	4.4	2.6	0.3

^a WHO annual air quality guideline, 10 µg m⁻³

^b Number of deaths/year

showed the highest estimated number of deaths associated with the excess $PM_{2.5}$. Through the application of the methodology recommended by WHO we found that the health impact, measured in terms of the excess mortality risk, was that more than 13,000 deaths per year were attributable to air pollution in the metropolitan regions under study.

Conclusions

In this study, we sampled urban atmospheric aerosol $PM_{2.5}$ for more than 1 year at sites with high traffic volumes within six Brazilian state capitals. The concentrations of $PM_{2.5}$ and black carbon were found to be lower in the summer months (November to February). Recife was the only city in which the profile differed, concentrations there remaining relatively constant throughout the year. As expected, meteorological conditions had a significant influence on pollutant concentrations, accounting for the peak concentrations.

Considering the trace element values obtained through EDXRF analysis, it was found that a high fraction of elements were derived from mineral dust, anthropogenic particles, S (a combustion product), and the burning of diesel, as well as from industries and residual oil combustion. Potassium also appeared in high concentrations, which is probably attributable to biomass burning in central and northern Brazil, including the burning of sugarcane in the process of ethanol production.

In five of the six cities evaluated, the annual mean $PM_{2.5}$ concentrations exceeded the air quality standard established for this pollutant by European and American legislation. The results of this study show the importance of implementing programs aimed at controlling the emissions of fine particulate matter in urban areas.

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