

# Characterization of urban aerosol in Campinas, São Paulo, Brazil

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## Abstract

A quantitative study was performed in Campinas, Brazil. Measurements were taken on an avenue with intense vehicle traffic in the city's downtown area from August 2003 to August 2004. A dichotomous sampler was employed for PM<sub>2.5</sub> and PM<sub>10</sub>. Samples were collected for 24 h at 3-day intervals. In addition, seasonal variations were investigated, using a MOUDI cascade impactor and VOC adsorption tubes, during a specific 5-day period in the summer of 2003 (December) and the winter of 2004 (August). The polycarbonate filters were analyzed by gravimetry, Particle Induced X-ray Emission (PIXE), ion chromatography and reflectance, to identify the mass concentration, elemental composition, ions and elemental carbon mass, respectively. The quartz filters were analyzed by gravimetry and thermal combustion carbon analysis to identify the mass concentration and carbon mass.

Results showed an annual mean of 20.85, 10.68 and 10.17  $\mu\text{g m}^{-3}$  for PM<sub>10</sub>, PM<sub>2.5</sub> and PM<sub>2.5-10</sub>, respectively. The cascade impactor provided mass distribution and revealed differences between the two seasons. The size distribution for chemical elements indicated soil-derived elements in the coarse fraction. PM winter concentrations were expected to be higher than those in summer, but that was not the case during the days of this study, when summer and winter concentrations were almost identical. The PIXE analysis revealed metals and metal compounds, soil-derived elements, sulfates, carbonates, chlorides and other anthropogenic air-borne particles, supposing molecules in their usual composition.

An analysis of the VOCs revealed benzene, toluene, *m,p*-xylene, *n*-hexane, 2-metilhexane and *n*-nonane. A mass balance analysis indicated different classes, among which elemental carbon was the most abundant, followed by organic carbon, soil elements and industrial sources.

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## 1. Introduction

Aerosols are introduced into the atmosphere from a variety of anthropogenic activities (transport, industri-

al activities, biomass burning and others) and natural sources (volcanic eruptions, sea salt, soil dust suspension, natural forest fires and others). Particles can influence the radiation budget in two ways: the first is by scattering and absorbing radiation, i.e., the direct effect, and the second is by changing optical properties, the life time and number of clouds, i.e., the indirect effect. Urban pollution is generally composed of soil-derived particles (PM<sub>10</sub> and PM<sub>2.5</sub>), particles from combustion processes, SO<sub>2</sub>, NO<sub>x</sub>, NH<sub>3</sub>, VOC and

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carbon. Sulfur dioxide, ammonia and nitrogen oxides are precursors of sulfuric acid, ammonium bisulfate, ammonium sulfate and ammonium nitrate particles that often constitute major fractions of  $PM_{2.5}$  and  $PM_{10}$ . Volatile organic compounds (VOCs) can participate in reactions, resulting in sulfuric acid, nitric acid, particle-phase organics and ozone, can have carcinogenic effects on human health (Pandis et al., 1992; Watson et al., 2001).

Most particle emissions from combustion sources are in the  $PM_{2.5}$  fraction. Fine particles can be directly emitted by sources or produced by condensation, coagulation and gas-to-particle conversion, common to combustion sources. Good descriptions of atmospheric aerosols can be found in Seinfeld and Pandis (1998), Finlayson-Pitts and Pitts (2000) and others.

Metropolitan Campinas (MC) encompasses 19 towns and cities with a total population of 2.3 million and an area of 3,654.6 km<sup>2</sup>. The region is a large industrial pole situated 100 km northwest of metropolitan São Paulo (MSP). Vehicles account for a significant part of the region's atmospheric pollution. The wide diversity of industrial activities, a significant part of them of a scientific and technological nature, represents a high volume of production destined for the domestic and global markets. Campinas, with its population of one million, stands out as the most important city of the region, followed by the industrial pole of Paulínia, which includes a petroleum refinery. Another contributing factor to the elemental carbon in the region's atmosphere is the burning of sugarcane in preparation for harvesting. In the 80's and 90's, the use of alcohol as a fuel and additive to gasoline has led to a decrease in CO and VOC emissions. Campinas has an average

temperature of 18–22 °C from May to September, and of 22–24 °C from October to March. The relative humidity may drop to as low as 15%, especially in September, creating poor conditions for the human health especially when associated with high pollution levels originated by unfavorable pollutant dispersion typical of this period. Over 80% of all the diseases in towns are produced by viruses and other microorganisms which enter the body through the respiratory organs. When the relative humidity is too low, viruses live longer and can enter our lungs easily as they float in the air with the dust. In the moist lungs they are activated and generate e.g. the common cold and other illnesses. Too dry air irritates the respiratory organs and, for instance, people suffering from asthma or allergies can have breathing difficulties. Dry air also makes the skin dry (Richards and Marriott, 1974; Huynh, 2001).

The winds are predominantly easterly and southerly during winter (the dry season). Fig. 1 pinpoints the location of MC and MSP in the state of São Paulo State and in South America.

The high populational, vehicular and industrial density contributes to increase the region's atmospheric pollution. Information about aerosol in the region of Campinas is scarce; most of it pertains to Paulínia, where industrial activity is more intense, indicating that in some instances the daily and annual standard are exceeded (Amorin, 2004; Tresmondi and Tomaz, 2004).

In this study, Campinas's atmospheric aerosol and VOCs were sampled for 1 year (26 Aug 2003 to 26 Aug 2004) and seasonal measurements were taken with a cascade impactor and a VOC collector in order to determine summer and winter concentrations. Different methodologies were employed to identify the mass

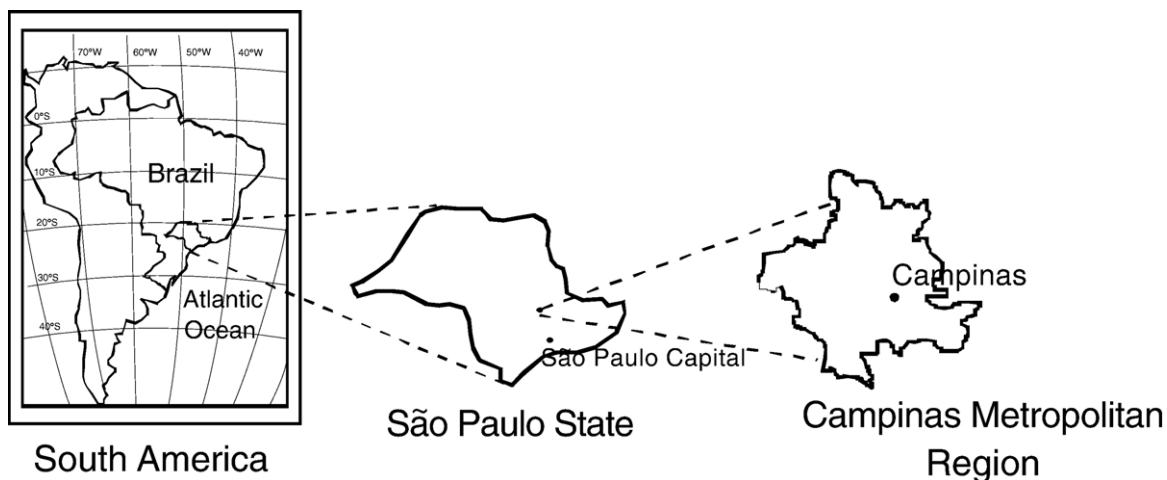


Fig. 1. Localization of sampling area.

and elemental concentration of particulate material. Annual and daily standard concentrations (CONAMA 03/1990 National Resolution (CETESB, 2006)) are 50 and 150  $\mu\text{g}\cdot\text{m}^{-3}$ , respectively.

## 2. Methodology

### 2.1. Sampling

The particles were collected in an urban area of Campinas using a dichotomous sampler equipped with polycarbonate and quartz filters for  $\text{PM}_{10}$  (aerodynamic diameter  $< 10 \mu\text{m}$ ) and  $\text{PM}_{2.5}$  (aerodynamic diameter  $< 2.5 \mu\text{m}$ ) to allow for the use of different analytical techniques (the sampling time was 24 h and the filters were changed every 3 days). Polycarbonate filter samples were collected every 6 days (the sampling time was 24 h), as were quartz filter samples, but sampling was done every 3 days, alternating only the type of filter. The dichotomous sampler used in this study was manufactured by Andersen Instruments Inc. This sampler is a low-flow rate (16.7 lpm) sampler that divides the air stream passing the  $10 \mu\text{m}$  inlet into two portions that are filtered separately. The samplers cut the 0– $10 \mu\text{m}$  total sampler into 0– $2.5 \mu\text{m}$  (fine) and 2.5– to  $10\text{-}\mu\text{m}$  (coarse) fractions that are collected on separate

filters. The sampler consists of two modules: the sampling module and the flow control module.

During specific periods of summer and winter, a cascade-type Micro-Orifice Uniform Deposit Impactor (MOUDI, model 100 MSP Corporation, Minneapolis) (Marple et al., 1986) was used to allow for a mass distribution study. The MOUDI has 10 different stages with varying nominal 50% cutoff (D-50) points: after-filter ( $0.02\text{-}\mu\text{m}$ ),  $0.1\text{-}\mu\text{m}$ ,  $0.18\text{-}\mu\text{m}$ ,  $0.32\text{-}\mu\text{m}$ ,  $0.56\text{-}\mu\text{m}$ ,  $1.0\text{-}\mu\text{m}$ ,  $1.8\text{-}\mu\text{m}$ ,  $3.2\text{-}\mu\text{m}$ ,  $5.6 \mu\text{m}$ ,  $10 \mu\text{m}$  and inlet ( $18 \mu\text{m}$ ). The MOUDI worked with  $0.4 \mu\text{m}$  pore diameters, Teflon-backed Nuclepore filters (after-filter diameter:  $37 \text{ mm}$ ; pore diameter:  $1 \mu\text{m}$ ), and a flow rate of 30 lpm was used.

Specific periods for MOUDI samplings: summer 2003 samplings were conducted during 8–12 December and winter 2004 samplings were conducted during 9–13 August. These samples were collected over a 5-day period, as described above, and each collection lasting for 12 h. The dichotomous sampler worked in parallel but for 24 h at a time. Volatile organic compounds were collected for some specific periods during these specific samplings (9–12 December 2003, summer and 10–13 August 2004, winter), using an adsorbent Perkin Elmer tube with TENAX TA resin (see Table 4). Fig. 2 presents a summary of sampling periods.

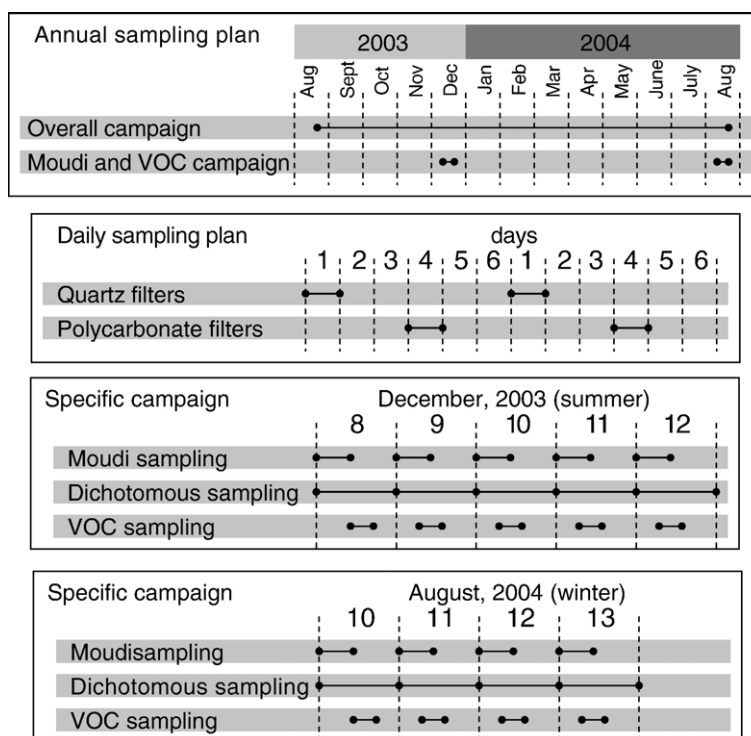


Fig. 2. Information of sampling periods.

## 2.2. Equipment and analyses

The polycarbonate filters were analyzed by gravimetry, Particle Induced X-ray Emission (PIXE), ion chromatography and reflectance to identify the mass concentration, elemental composition, ions and elemental carbon mass, respectively. The quartz filters were analyzed by gravimetry and thermal combustion carbon analysis to identify the mass concentration and organic carbon mass. Gravimetry was performed using a Mettler balance with a nominal precision of 1  $\mu\text{g}$ . Blank filters were used for every stock purchased for sampling and the corresponding blank concentrations were subtracted from each sample.

PIXE (Johansson et al., 1995) X-ray spectra for fine fractions were accumulated for 600 s with measured concentrations of Al, Si, P, S, Cl, K, Ca, Ti, V, Cr, Mn, Fe, Ni, Zn, Ga, Br, Zr and Pb. The spectra generated by PIXE were analyzed using AXIL software (Van Espen, 1994).

Ion chromatography was performed for  $\text{Na}^+$ ,  $\text{NH}_4^+$ ,  $\text{K}^+$ ,  $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$  in a Metrohm model 761 Compact IC chromatograph.

Using the reflectance technique, an elemental carbon analysis was performed with a Diffusion Systems model M43D smoke stain reflectometer. The quartz filters were also analyzed by a thermo method, in which the organic carbon analysis is based on  $\text{CO}_2$  formation considering the oxidation of carbonaceous compounds at different temperature intervals. A sample was heated to 450  $^\circ\text{C}$  for 6 min for the organic carbon analysis, then to 700  $^\circ\text{C}$

for elemental carbon analysis and the results of the two methods were compared for EC in quartz filters.

The equipment used for analysis was a Dohrmann DC-85 carbon analyzer with an adapted oven. For organic carbon analysis the analytical group decided on 450  $^\circ\text{C}$  with 2%  $\text{O}_2$ , with fast burn in order to minimize pyrolytic production of elemental carbon. A fraction of 0.242  $\text{cm}^2$  of the filter is oxidized in an oxidation oven under a 2%  $\text{O}_2/\text{Ar}$  flux firstly to 450  $^\circ\text{C}$  in order to determine organic carbon and after to 700  $^\circ\text{C}$  for elemental carbon. Carbonaceous matter total oxidation is completed by the passage through a bed of solid  $\text{CuO}$ .  $\text{CO}_2$  generated by passage through a wash bottle containing phosphoric acid is quantified by an infrared detector. Some tests performed in the laboratory indicated an insignificant loss of organic material.

AVOC tube analysis of the samples was done, with the samples injected by thermal desorption (ATD-400-Perkin Elmer) and subsequently transferred for identification and quantification to an analytical system composed of a mass spectrometer coupled to a gas chromatograph with flame detector ionization (GC/MS/FID).

## 3. Results and discussion

### 3.1. Concentration and characterization

Fig. 3 shows  $\text{PM}_{10}$  concentrations during the sampling period. The concentrations were higher in winter (August and September) than in summer.

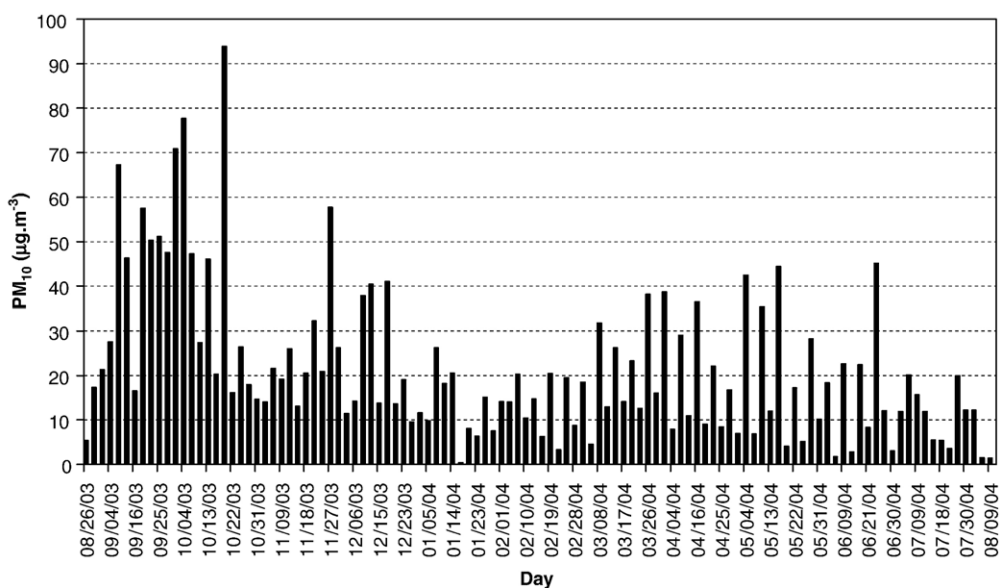


Fig. 3.  $\text{PM}_{10}$  mean annual concentrations ( $\mu\text{g}\cdot\text{m}^{-3}$ ).

Annual and daily standard concentrations (CONAMA 03/1990 National Resolution) ( $50$  and  $150 \mu\text{g m}^{-3}$ , respectively) were not exceeded and the annual mean was  $20.85 \pm 16.61 \mu\text{g m}^{-3}$  (minimum =  $1.38 \mu\text{g m}^{-3}$  and maximum =  $93.86 \mu\text{g m}^{-3}$ ),  $10.68 \pm 8.25 \mu\text{g m}^{-3}$  (minimum =  $0.23 \mu\text{g m}^{-3}$  and maximum =  $44.76 \mu\text{g m}^{-3}$ ) and  $10.17 \pm 10.00 \mu\text{g m}^{-3}$  (minimum =  $0.15 \mu\text{g m}^{-3}$  and maximum =  $62.31 \mu\text{g m}^{-3}$ ) for  $\text{PM}_{10}$ ,  $\text{PM}_{2.5}$  and  $\text{PM}_{2.5-10}$ , respectively.

Table 1 presents the elemental analysis by PIXE, expressed as annual means in  $\text{ng m}^{-3}$ . Soil-derived elements presented high concentrations, although anthropogenic elements also appeared. Vanadium (V) is a product of diesel and oil burn and sulfur (S) derives from combustion processes. The latter element derives from gas-to-particle conversion and, in gaseous form, can be related to (silicon dioxide)  $\text{SO}_2$  and (sulfidric acid)  $\text{H}_2\text{S}$ , the former a product of fossil fuel combustion and the latter from organic matter. Manganese (Mn) can be related to industrial processes, while iron (Fe) and zinc (Zn) in the fine fraction are associated with combustion processes. Potassium (K) is normally associated with biogenic sources.

Some authors, such as Boueres and Orsini (1981) and Andrade et al. (1994), studied urban aerosols in Brazil and their possible sources. The atmospheric pollution of Campinas has not previously been subjected to this type of analysis, but a comparison of these findings with others reported for São Paulo (Castanho and Artaxo, 2001;

Table 1  
PIXE annual means ( $\text{ng.m}^{-3}$ )

Element	Mean	Stdev
Al	50.3	2.9
Si	49.1	2.0
P	3.7	0.6
S	248.0	7.7
Cl	3.2	0.6
K	51.3	1.6
Ca	20.3	0.8
Ti	22.9	2.6
V	3.4	0.7
Cr	4.2	0.7
Mn	14.8	1.6
Fe	585.1	59.1
Ni	4.3	0.6
Cu	18.1	1.9
Zn	80.0	12.1
Se	0.1	0.0
Br	1.3	0.5
Sr	0.4	0.1
Zr	0.2	0.1
Pb	3.6	0.4

Table 2  
Meteorological conditions during MOUDI samplings

	Relative humidity (%)	Temperature ( $^{\circ}\text{C}$ )	Wind speed ( $\text{m.s}^{-1}$ )	Pressure (mb)	Wind direction (degrees)
<b>Summer</b>					
12/08/2003	66.21	19.84	1.50	937.00	SSW
12/09/2003	93.45	20.74	1.50	945.02	SSW
12/10/2003	83.08	23.17	0.88	945.90	ESE
12/11/2003	82.77	25.06	1.08	944.33	SE
12/12/2003	86.77	22.61	1.24	946.08	SSE
Mean	82.46	22.29	1.24	943.67	
<b>Winter</b>					
08/09/2004	66.81	13.80	2.58	959.07	ESE
08/10/2004	71.49	15.78	2.01	958.16	ESE
08/11/2004	71.57	15.88	1.39	956.60	SE
08/12/2004	68.14	15.44	3.18	959.08	ESE
08/13/2004	64.50	15.62	2.13	959.41	ESE
Mean	68.50	15.30	2.26	958.46	

Miranda et al., 2002; Miranda and Andrade, 2004) revealed similar results, albeit of lower magnitudes.

### 3.2. Seasonal variations

As mentioned above, two measuring campaigns were conducted: summer 2003 samplings during 8–12 December and winter 2004 samplings during 9–13 August in order to study possible differences between the two seasons. PM winter concentrations were expected to be higher than those in summer, but that was not the case during the days of this study, when summer and winter concentrations were almost identical. Table 2 shows daily average meteorological conditions for the periods. In the summer period, wind predominated from rural regions, increasing the coarse fraction of particulate; in the winter, the wind predominated from industrial regions, increasing S, for example.

Probably summer concentrations in the period were higher than normal because of high wind speeds (exception for December, 10), pressure increase during the week and relative humidity fall.

Fig. 4 shows the mean concentrations in the two seasons in each impactor stage. Except for particles smaller than  $0.1 \mu\text{m}$ , the summer concentrations were higher. Sulfur and other small particles can contribute to this situation since the element had higher concentrations in the winter and belongs to fine fraction. In a separate analysis of diurnal and nocturnal samples (Fig. 5a and b), the size distributions showed higher concentrations during the day in summer and winter (exception for  $3.2 \mu\text{m}$  in the winter), and higher concentrations of coarser stages during the day (stages with cut diameter above  $1 \mu\text{m}$ ). This finding can be explained

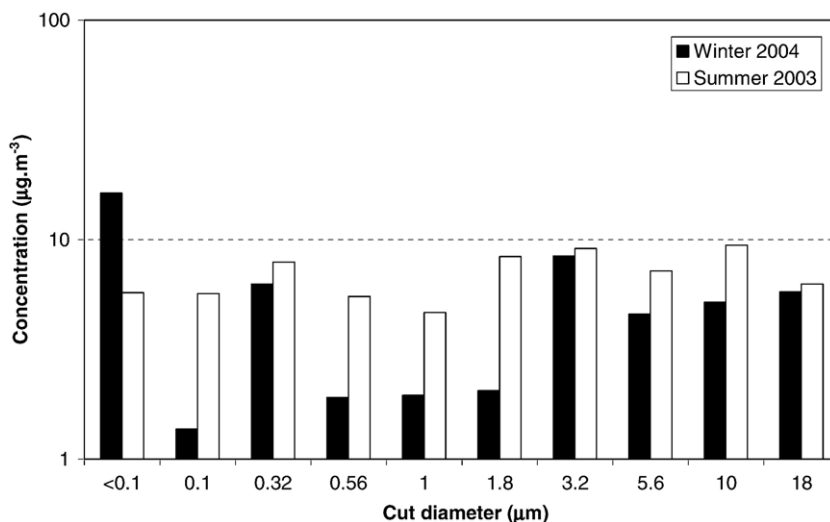


Fig. 4. Mean size distributions for summer and winter samplings with MOUDI impactor.

by analyzing the PIXE results; Table 1 shows both anthropogenic and non-anthropogenic elements. Comparing the diurnal and nocturnal concentrations of two seasons, higher concentrations of soil-derived elements were observed during the day in summer and winter. As Fig. 6 and other works (Miranda et al., 2002; Miranda and Andrade, 2004) indicate, these elements belong to the coarse fractions.

### 3.3. VOC analysis

Samples were collected from 7:00 to 9:00 A.M., during morning peak traffic and in parallel to the MOUDI samplings, as indicated in Table 3. Among the species analyzed during the two periods, toluene, *n*-hexane and benzene showed the highest concentrations. Since the samplings were situated in a region of intense traffic of vehicles, it was expected that the ambient VOC concentrations were mainly affected by emissions from urban activities.

A comparison of the summer and winter concentrations of these elements revealed higher concentrations in winter. High concentrations of other elements such as 3-methylpentane, cyclohexane and *m,p*-xylene were found during winter. Anthropogenic sources of VOCs include evaporation of solvents and gasoline, petrochemical manufacturing, oil refining and motor vehicle exhaust. Benzene, toluene, xylenes and pentanes can be related to liquid gasoline, which represent unburned gasoline due to misfiring and other engine malfunctions. Industrial emissions are represented by *n*-hexane 3-methylpentane and others also interpreted as industrial emissions. It was not possible to analyze the same species in both seasons,

but our findings give one an idea of the concentrations in Campinas, since these data have not so far been studied extensively. An investigation of the daily cycle carried out on December 10 (summer) showed the highest concentrations occurring between 7:00 and 9:00 A.M., during the morning peak traffic (Fig. 7) and from 1:00 to 3:00 P.M. (a sensible increase in this period), during the lunch hour and return to work. Buzcu and Fraser (2006) analyzed 54 VOCs from three monitoring sites in the heavily industrialized Houston Ship Channel and the interested reader can find a good description of VOCs species and sources.

Martins et al. (2007) compared results from their VOC samplings and others around the world. Comparing these results with other Brazilian sites, benzene and ethylbenzene were comparable with concentration in Brazilian megacities like São Paulo and Porto Alegre, but toluene, *m,p*-xylene and *o*-xylene concentrations were lower. For example, Colón et al. (2001) found means of 4.8, 45.1, 15.6, 30.7 and 7.8  $\mu\text{g m}^{-3}$  in São Paulo for benzene, toluene, ethylbenzene, *m,p*-xylene and *o*-xylene, respectively.

Several studies of atmospheric pollution have been conducted in urban areas, e.g., Na et al. (2001) compared industrial and downtown VOCs concentrations and found the highest for the industrial site. Downtown concentrations of ethylene, propylene, acetylene, butanes and pentanes, closely related to vehicle exhausts and evaporative emissions, were high. The concentrations of ethylene, propylene, vinyl chloride, cyclohexane and tetrahydrofuran largely associated with petrochemical industries were high at the industrial site (most of them not evaluated in this study).

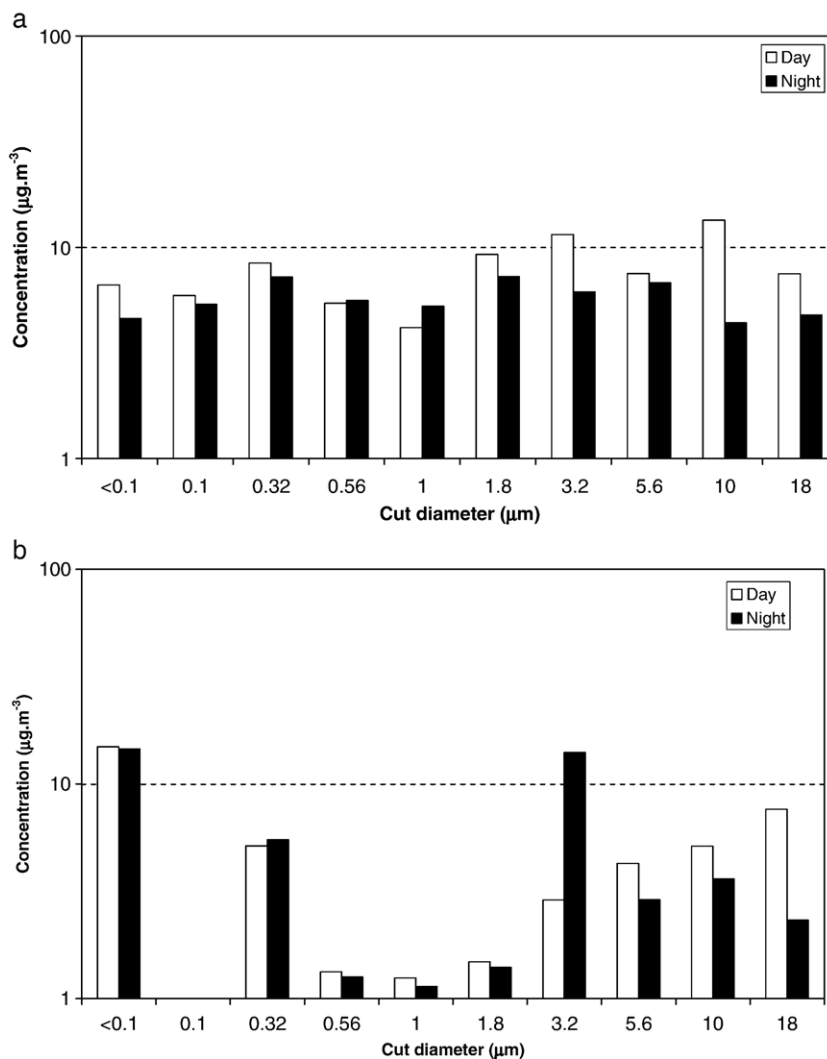


Fig. 5. Mean Size distributions for day and night samplings in summer (a) and winter (b) with MOUDI impactor.

### 3.4. Carbon analysis

Considering that the sampling area was close to an avenue with heavy traffic, the analysis of carbon is important, since organic and elemental carbon are very abundant species in motor vehicle exhaust. Table 4 shows mean carbon concentrations and percentage of total mass. Elemental carbon predominated in fine fractions, representing 31% of the total fine mass. The quartz filters were analyzed by the reflectance and thermal techniques, allowing for a comparison of the two methods (for elemental carbon). Fig. 8 presents the results for the fine and coarse fractions. Although the techniques involve different methodologies, they showed a good correlation for fine fraction. The reflectance technique showed higher results for the fine fraction than did the thermal method

(angular coefficient of 0.90), whereas the opposite held true for the coarse fraction (angular coefficient of 0.5). This may be due to the fact that, by the thermal method, elemental carbon is analyzed after organic carbon (first burn at 450 °C for organic carbon and subsequently at 700 °C for elemental carbon, in the same filter) and in the case of the fine fraction, in which elemental concentrations are higher, this may result in a loss of the element's intensity, due to the first burn. However, in the coarse fraction elemental carbon concentrations are lower and consequently first burn probably does not affect results.

### 3.5. Mass balance

To obtain the mass balance results, the fine fraction of the particulate material was analyzed by the three

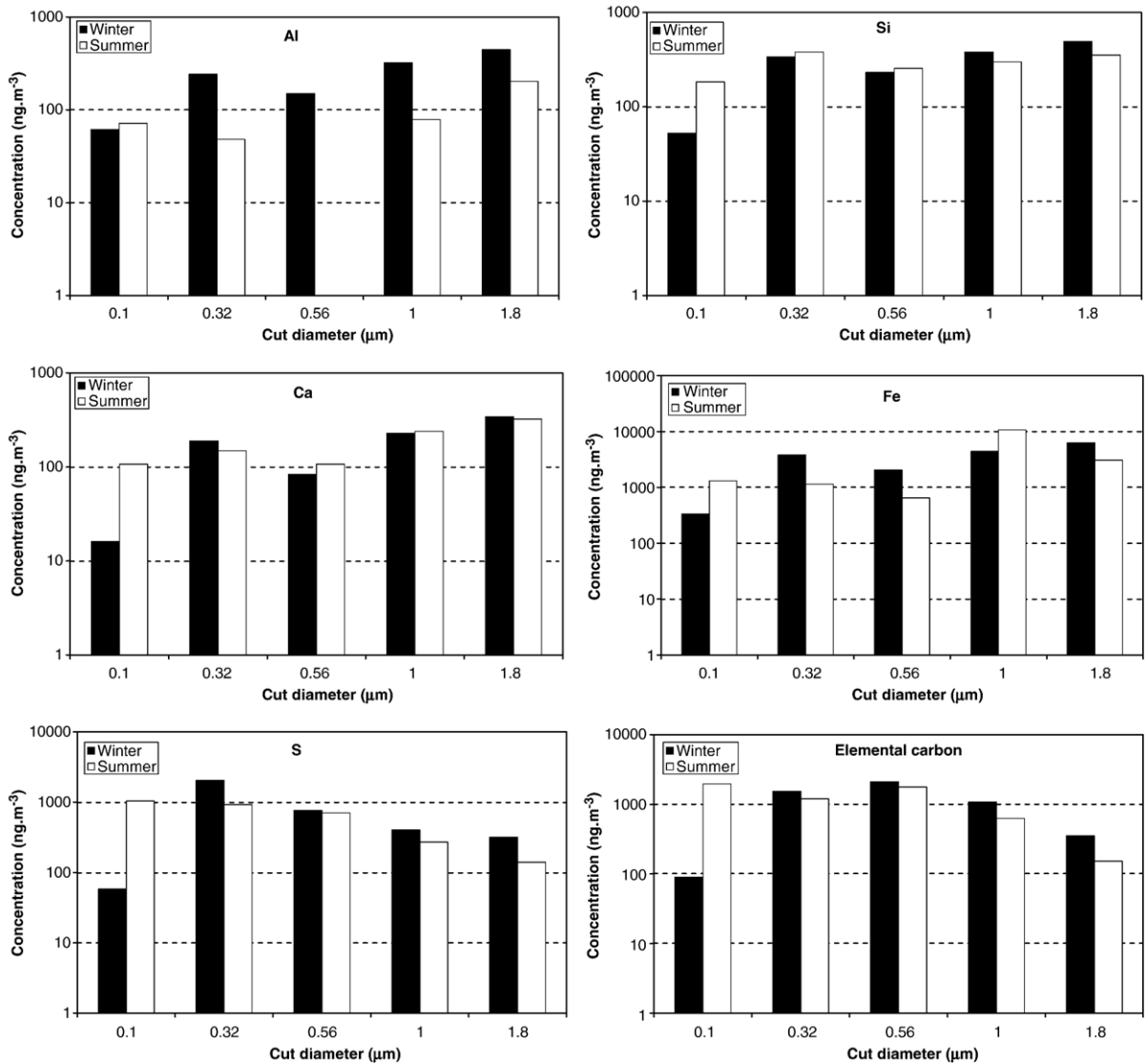


Fig. 6. Mean size distributions for elements in the winter and summer with MOUDI impactor.

techniques (gravimetry, PIXE, and ion chromatography). The elements analyzed by PIXE were considered in their more common oxidative forms. Elements produced during combustion usually appear in the form of oxides such as magnesium, aluminum, titanium, copper, zinc, potassium, vanadium, nickel, and manganese oxides, silicon dioxide, calcium and iron trioxides, phosphorus pentoxide, ammonium sulfate, and sodium chloride. Fig. 9 presents the results. In view of the site where samples were collected, elemental carbon was the most abundant, followed by organic carbon, soil elements and industrial sources.

Three factors were identified by Varimax rotation factor analysis (Table 5), explaining 82.67% of the results. The first factor involved soil-derived elements ( $\text{Al}_2\text{O}_3$ ,  $\text{SiO}_2$ ,  $\text{CaO}_3$ ,  $\text{TiO}$ ,  $\text{Fe}_2\text{O}_3$ ,  $\text{Sr}$ ,  $\text{Zr}$ ), relating to road dust resuspended by foot and vehicle traffic and even to public gardens close to the downtown sampling site. The source of  $\text{Sr}$  and  $\text{Zr}$  was undefined. The second factor involved industrial and vehicular sources ( $(\text{NH}_4)_2\text{SO}_4$ ,  $\text{Cu}_2\text{O}$ ,  $\text{ZnO}$ ,  $\text{P}_2\text{O}_5$ ,  $\text{Pb}$ ,  $\text{BC}$ ).  $\text{S}$  originates from the combustion of fossil fuels and other sources, as mentioned above.  $\text{Cu}$  can be emitted by vehicles, since it is related to brakes, while the source of  $\text{Pb}$  is probably industrial, since gasoline no



Table 3  
Volatile Organic Compounds concentrations for summer and winter samplings ( $\mu\text{g}\cdot\text{m}^{-3}$ )

	09/Dec 07–09hs	Summer 10/Dec 07–09hs	11/Dec 07–09hs	12/Dec 07–09hs	10/Aug 07–09hs	Winter 11/Aug 07–09hs	12/Aug 07–09hs	13/Aug 07–09hs
<i>n</i> -pentane	5.71	5.22	7.94	5.05	1.03	0.86	1.18	1.14
3-methylpentane					1.34	11.07	1.19	13.33
<i>n</i> -hexane	8.78	11.04	10.37	6.28	14.66	39.38	15.63	18.62
Methylcyclopentane					5.79	7.39	4.64	4.64
Benzene	4.65	5.43	2.29	1.30	10.34	6.07	11.11	11.31
Ciclohexane					7.78	6.47	6.20	7.76
2-methylhexane	2.67	2.73	17.22	0.98	3.49	0.80	3.21	3.11
3-methylhexane					2.57	0.50	2.29	2.27
2,2,4-TMP					2.30	0.43	2.10	1.91
<i>n</i> -heptane	3.54	3.38	2.88	0.67	4.84	0.98	3.35	4.05
Methylciclohexane					1.86	0.10	1.83	1.72
Toluene	10.68	14.98	10.66	2.05	16.92	6.03	13.21	14.97
<i>n</i> -octane	2.37	2.51	2.00	0.28	2.93	0.37	2.77	2.86
Clorobenzene					4.10	2.06	3.33	3.70
Ethylbenzene					7.87	2.28	6.71	6.40
<i>m,p</i> -xylene					12.54	1.91	11.85	12.00
Estirene					2.10	0.90	1.83	2.24
<i>o</i> -xylene					4.14	0.68	4.03	4.13
<i>n</i> -nonane	3.01	3.44	3.14	0.45	4.03	0.58	3.93	3.45
Cumene	0.25	0.17	0.15	0.10	0.38	0.24	0.30	0.36
1,3,5-TMB					1.37	0.52	1.41	1.52
1,2,4-TMB					4.61	0.38	4.75	5.77
<i>n</i> -decane	1.11	1.08	1.07	1.81	1.29	0.42	0.89	1.32
Mix-diethylbenzenes	1.03	0.72	1.59	2.87	0.57	1.16	1.29	1.26

longer contains this element. The third factor was (Br, NaCl, K<sub>2</sub>O) associated with marine and vegetal sources (Andrade et al., 1994; Castanho and Artaxo, 2001; Miranda et al., 2002; Miranda and Andrade, 2004).

Analyzing wind direction throughout the sampling year, the predominant direction was found to be SE,

SSE, i.e., the direction of the city of São Paulo, located 100 km from Campinas. Higher PM<sub>10</sub> concentrations appeared in this direction, with higher concentrations of industrial elements, suggesting the possible contribution of pollution from São Paulo. This also appeared to be a possibility when marine particles were found in

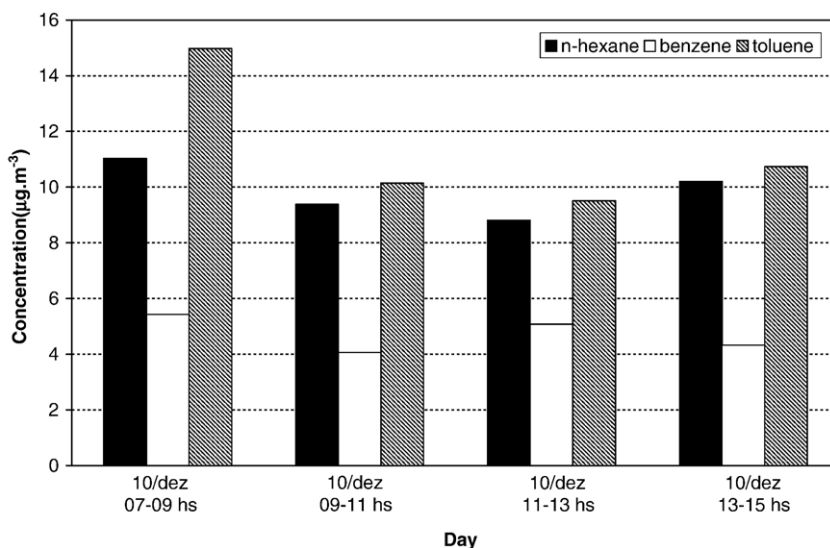


Fig. 7. Daily variations for toluene, benzene and *n*-hexane.

Table 4  
Carbon concentrations

	Organic carbon ( $\mu\text{g}\cdot\text{m}^{-3}$ )	Elementar carbon ( $\mu\text{g}\cdot\text{m}^{-3}$ )	% OrgC	% EC
Fine fraction	2.54	3.70	19	31
Coarse fraction	1.02	1.10	6	8

the analysis, since the Atlantic Ocean is situated SE of São Paulo and Campinas (Fig. 1). Lower concentrations appeared in the SW and SSW directions, which predominantly showed soil-derived elements.

4. Conclusions

A quantitative study was conducted in downtown Campinas, in the state of São Paulo, Brazil. The aerosol in Campinas’s atmosphere was sampled over a one-year

period (August 26, 2003 to August 26, 2004) and seasonal measurements were taken with a cascade impactor and a VOC collector to identify summer and winter concentrations. The filters were analyzed by gravimetry, Particle Induced X-ray Emission (PIXE), ion chromatography, reflectance and thermal combustion carbon analysis to identify the mass concentration, elemental composition and elemental carbon mass, respectively. Standard annual and daily concentrations ( $50$  and  $150 \mu\text{g m}^{-3}$ , respectively) were not exceeded, and the annual mean concentration was found to be  $20.85$ ,  $10.68$  and  $10.17 \mu\text{g m}^{-3}$  for  $\text{PM}_{10}$ ,  $\text{PM}_{2.5}$  and  $\text{PM}_{2.5-10}$ , respectively. The seasonal measurements taken in the summer of 2003 (December) and in the winter of 2004 (August) revealed almost identical concentrations, contrary to what was expected (higher concentrations in winter due to meteorological conditions). Due to the

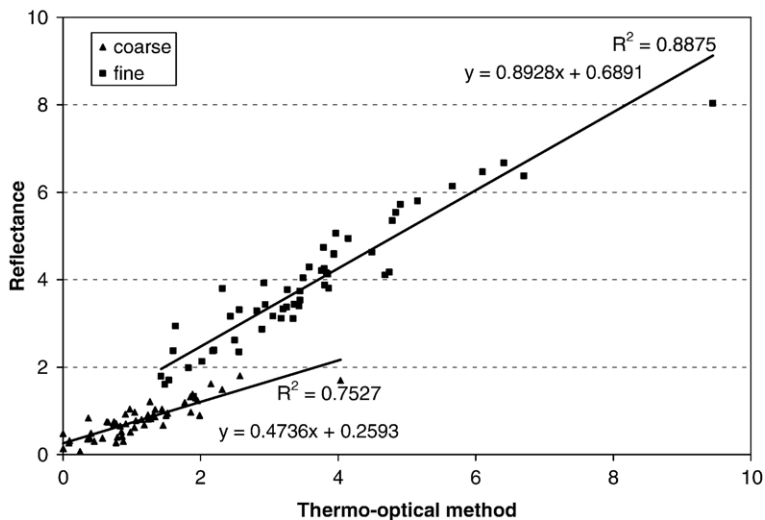


Fig. 8. Carbon analysis comparison for thermal and reflectance methods.

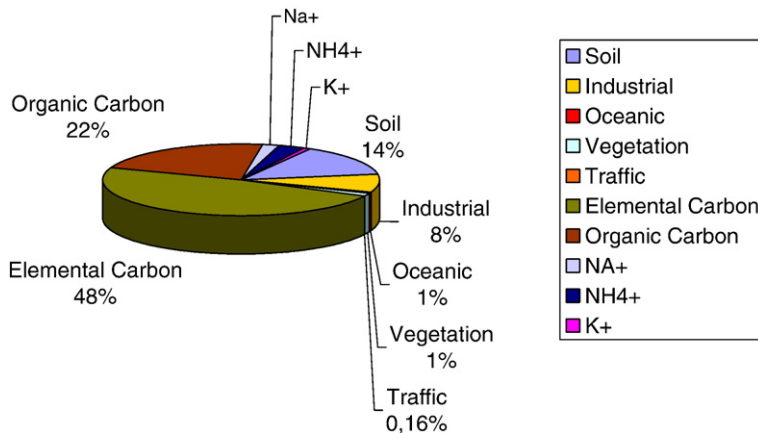


Fig. 9. Mass balance by source of fine mode concentrations ( $\text{PM}_{2.5}$ ) for all the period.

Table 5  
Principal Component Analysis results

	Factor 1	Factor 2	Factor 3
Al <sub>2</sub> O <sub>3</sub>	<b>0.84</b>	0.18	0.40
SiO <sub>2</sub>	<b>0.84</b>	0.20	0.38
CaO <sub>3</sub>	<b>0.82</b>	0.49	0.17
TiO	<b>0.83</b>	0.36	0.39
Fe <sub>2</sub> O <sub>3</sub>	<b>0.78</b>	0.44	0.38
Sr	<b>0.77</b>	0.41	0.20
(NH <sub>4</sub> ) <sub>2</sub> SO <sub>4</sub>	0.53	<b>0.74</b>	0.13
Cu <sub>2</sub> O	0.44	<b>0.77</b>	0.31
ZnO	0.08	<b>0.88</b>	0.35
Br	0.14	0.30	<b>0.76</b>
P <sub>2</sub> O <sub>5</sub>	0.61	<b>0.70</b>	0.21
MnO <sub>2</sub>	0.51	0.24	0.55
Zr	<b>0.89</b>	0.20	0.14
Pb	0.02	<b>0.77</b>	0.45
NaCl	0.23	0.18	<b>0.84</b>
K <sub>2</sub> O	0.38	0.04	<b>0.71</b>
VO	0.60	<b>0.73</b>	0.06
NiO	0.54	<b>0.75</b>	0.07
BC	0.28	<b>0.70</b>	0.04
Eigenvalues	12.29	1.87	1.55
% variance	64.68	9.82	8.16
% cumulative variance	64.68	74.50	82.67

location of the sampling site, the mass balance results showed elemental carbon as the most abundant, followed by organic carbon, soil elements and industrial sources. An analysis of wind directions suggested a possible contribution from the city of São Paulo (located 100 km from Campinas), with higher PM10 concentrations when southeasterly winds predominated. The VOC analysis indicated that the principal contributors to the atmospheric pollution were benzene, toluene, *m*, *p*-xylene, *n*-hexane, 2-metilhexane and *n*-nonane.

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