Polycyclic aromatic hydrocarbons and their molecular diagnostic ratios in urban atmospheric respirable particulate matter

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Abstract

Atmospheric concentrations of polycyclic aromatic hydrocarbons (PAHs) in Santiago de Chile city were evaluated to study particulate PAHs profiles during cold and spring weather periods. Urban atmospheric particulate matter PM10 was collected using High Volume PM10 samplers. Fifteen samples of 24 h during austral winter and 20 samples of 24 h during spring, 2000 were collected at two sampling sites (North–East and Central areas of the city) whose characteristics were representative of the prevailing conditions. Seventeen PAHs were quantified and total PAHs concentration ranged from 1.39 to 59.98 ng m^{-3}, with a seasonal variation (winter vs. spring ratio) from 0.5 to 12.6 ng m^{-3}. Molecular diagnostic ratios were used to characterize and identify PAHs emission sources such as combustion and biogenic emissions. Results showed that the major sources of respirable organic aerosol PM10 in Santiago are mobile and stationary ones.

Keywords: Polycyclic aromatic hydrocarbons; PM10; Molecular diagnostic ratios; Santiago de Chile

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1. Introduction

Atmospheric aerosols are ubiquitous in the troposphere and play an important role in climate and atmospheric chemistry. They include inorganic and organic chemical species, which could have harmful effects on human health (Charlson et al., 1992; King et al., 1993; Finlayson-Pitts and Pitts, 1997).

Polycyclic aromatic hydrocarbons (PAHs) are one of the several hundred organic compounds that have been identified in the particulate matter. They are products of incomplete combustion formed during the burning or pyrolysis of organic matter. Some of them are among the strongest known carcinogens (IARC, 1984; Finlayson-Pitts and Pitts, 1997, 2000). Their widespread presence is due to their emissions from a wide range of combustion sources including gasoline and diesel engines (Benner et al., 1989; Westerholm et al., 1991), biomass burning of agricultural and forest (Jenkins et al., 1996; Finlayson-Pitts and Pitts, 2000) and wood combustion (Finlayson-Pitts and Pitts, 2000).

Atmospheric PAHs are partitioned between the particulate and the gaseous phases. This gas–particle partition has strong dependence on PAHs' molecular weight. Low molecular weight PAHs have higher concentrations in the vapor phase while high molecular weight ones are often associated with particles (Bi et al., 2003). Nevertheless, the recognized carcinogenic PAHs are mostly associated with particulate matter (Cautreels and VanCawenberghe, 1978; Lyall et al., 1988; Pankow and Bidleman, 1999; Lee and Tsay, 1994; Foreman and Bidleman, 1987; Yamasaki et al., 1982). It was also seen that PAHs have their highest concentration in the respirable size range of airborne particulate matter (Pistikopoulos et al., 1990; Venkataraman and FriedIander, 1994; Finlayson-Pitts and Pitts, 1997, 2000). Because of the ubiquitous nature of atmospheric PAHs and their highest levels in urban environment, the risk to human exposure is high for the inhabitants of the cities.

Molecular diagnostic ratios can be used to identify contributions of sources such as combustion and biogenic emissions (Alves et al., 2001; Caricchia et al., 1999; Cereceda-Balic et al., 2002; Gogou et al., 1996; Kavouras et al., 1999; Pio et al., 2001). Previous studies of PAHs carried out in Santiago's airborne particulate matter consider TSP (total particulate matter) (Gil and Adonis, 1996), PM5 (particulate matter <5 μm) (Gil et al., 1997), PM2.5 (particulate matter <2.5 μm) (Kavouras et al., 1999; Cereceda-Balic et al., 2002) and PM10 (particulate matter <10 μm) (Didyk et al., 2000). On the other hand the mutagenic activity of the particulate matter had been studied by Gil et al. (1991), Adonis and Gil (1993), Silva et al. (1992), Quiñones-Sepúlveda and Gil (1995) and Gil and Adonis (1996).

The aim of this study is to identify and quantify the most important PAHs occurring in the PM10 of Santiago de Chile, during winter and spring, and their possible sources using the molecular diagnostic ratios.

2. Geographic location

Santiago, the capital of Chile, is located in a fairly restricted basin on the western foothills of the Andes, with the anticiclonal subtropical predominance ($32°55'$ and

34°19′S, 69°46′ and 71°39′W). The geographic land of the region, 15 479 km^2, has 87.5% mountains and 3.3% valleys. The urban area is surrounded by hills and mountains that range from 500 to 2500 m above sea level. Air circulation is therefore limited and dispersion mechanisms are mainly related to vertical circulation that prevails during summer months (December–March), being inversion limit layers higher in some sections of the basin airshed. In winter, with thermal inversion heights below the airshed, contaminant accumulation increases and air quality can quickly deteriorate (Sandoval et al., 1993). Mean temperature during sampling in winter 2000 was 7.5 °C (5.2–9.8 °C) and during sampling in spring 2000 was 14.7 °C (13.1–16.3 °C). The city has a population of more than 6 000 000 inhabitants and about 1 000 000 motor vehicles (INE, 2002), also industries and a power plant are located in the city.

3. Experimental and analytical techniques

3.1. Sampling sites

Samples of urban PM10 were collected at Providencia and Las Condes, two of the nine monitoring stations belonging to the Air Quality Monitoring Network managed by the Environmental Health Service for the Metropolitan Region (SESMA) (Fig. 1). At these sites SESMA routinely measures O_3, NOx, CO, SO_2, PM10, PM2.5 and meteorological parameters. Providencia is close to the central area of the city and is characterized by a high traffic density. Las Condes is located at the northeast side of the city in the direction of the predominant winds; traffic is much less than in Providencia.
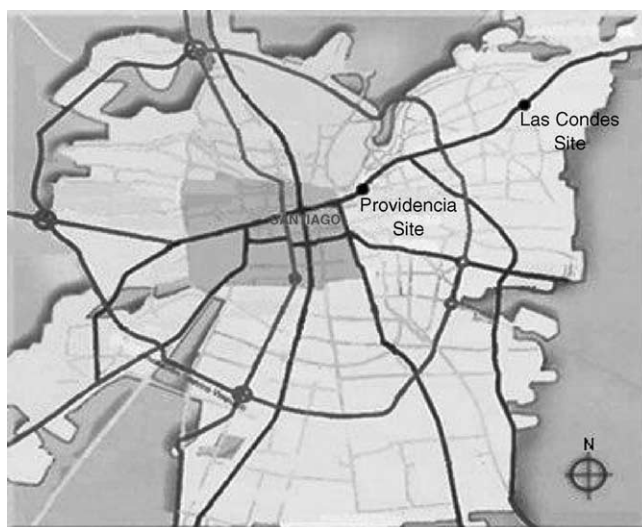

Fig. 1. Map of the Metropolitan Region of Santiago, Chile, with the location of the sampling sites, named 1: Providencia and 2: Las Condes. Source: http:geochile.cl.

3.2. Sample collection

PM10 was collected on quartz fibre filters (20×25 cm) with a High-Volume air sampler (Model Graseby Andersen) equipped with PM10 size-selective inlets. The samplers operated at a constant flow rate of 1.13 m^3 min^{-1} for periods of 24 h. Samples were collected during 7–19 July (winter) and from September 27 to October 7 (spring) 2000. Sampling periods extended from 9:00 am of one day to 9:00 am of the next day. A total of 7 samples in Providencia and 8 samples in Las Condes were collected during winter and 10 samples during spring at each site. After sampling, the filter was removed from the sampler, folded with the particulate matter inside, wrapped in an aluminum foil and stored in a freezer (-18 °C) until the analysis.

3.3. Materials

Organic solvents of analytical grade were purchased from Merck and Co. (Hohenbrunn, Germany) and Fisher Scientific International (Pittsburgh, Pennsylvania). Anhydrous sodium sulphate (analytical grade, washed with CH_2Cl_2 and activated in an oven at 400 °C for 4 h) was obtained from Merck. Silica gel 75–150 μm (extracted with CH_2Cl_2 for 6 h, activated at 130 °C in an oven for 24 h and stored in a dessicator until use) was obtained from Wako (Osaka, Japan). Multi or individual PAHs standards were purchased from Supelco (Bellefonte, PA, USA) and Ultra-Scientific Inc. (North Kingston, RI, USA). A standard reference sample of Diesel Particulate Matter (SRM 1650) and a standard reference sample of Urban Dust (SRM 1649) from National Institute of Standards and Technology (NIST) were used. Glassware used for extraction and analyses was rinsed with methanol and hexane just before use.

3.4. Sample preparations and silica gel chromatography

Before the chemical analysis each filter with particulate matter was removed from the freezer and stored in a dark and closed chamber with controlled temperature and humidity for 24–48 h. Then they were weighed in order to obtain the mass of PM10 collected.

A summarized analytical procedure used in this study is as follows: the filter was cut into small pieces and soxhlet extracted with dichloromethane for 24 h. Extracts obtained were concentrated in volume using a rotary evaporator at a temperature between 30 and 45 °C and Phenanthrene-d10 added. Then they were fractionated using a 30 cm×1 cm i.d. glass column chromatography with anhydrous silica gel in hexane. Each sample was placed on the top of the column and eluted with different mixtures of solvents: *n*-hexane, *n*-hexane/CH_2Cl_2, 6:4; CH_2Cl_2; acetone 30%/*n*-hexane (v/v). The different eluted fractions were evaporated to small volume (<1 mL) using a rotary evaporator at a temperature between 30 and 45 °C and then under flow of nitrogen, added with internal standards and finally adjusted to exactly 1 mL. Simultaneously, analytical blanks of the methodology were done. The methodology was validated using NIST standards SRM 1650 and 1649 (Sienra, 2002; Sienra et al., 2002).

3.5. Analysis of PAHs

All fractions were analyzed using gas chromatography with mass selective detection (GC-MS) using a Hewlett-Packard (HP) 6890 gas chromatograph (GC) coupled to a HP-5973 mass spectrometer. The GC was equipped with a HP-5MS capillary column (5% Phenyl-methylpolysiloxane) 30 m×0.25 mm i.d.×0.25 μm film thickness. The chromatographic conditions were as follows: injector temperature, 280 °C; ion source temperature, 230 °C; temperature program: 40 °C (1 min), 40–140 °C at 20 °C/min, 140–300 °C (10 °C/min), 300 °C (2 min). The carrier gas was Helium at a constant flow rate of 1.5 mL/min. A sample of 1 μL was injected with splitless mode. Chromatographic peaks of samples were identified by GC-MS analysis and coinjection with authentic standard compounds. A quantitative analysis was performed using a single ion monitoring (SIM) method at electron energy, 70 eV. The molecular ion of each PAH was used for SIM (Sienra, 2002; Sienra et al., 2002).

A recovery test was performed on 10 PAHs using exactly the method described before (Sienra, 2002; Sienra et al., 2002). The mean PAHs recovery was about 87% with C.V. of 12%. The mean quantification limit was 0.0029 ng m^{-3} and the mean detection limit was 0.00086 ng m^{-3}. Detection limit (DL) and quantification limit (QL) were calculated taking into account 3 and 10 times respectively the ratio of the heights obtained for noise and for peak of the lowest standard concentration. The PAHs concentrations were corrected for recovery efficiency during extraction and silica gel chromatography.

The concentrations of the following compounds were determined: naphthalene (Nap), acenaphtylene (Acy), acenaphthene (Ace), fluorene (Flu), phenanthrene (Phe), anthracene (Ant), fluoranthene (Fl), pyrene (Py), benzo(*a*)anthracene (BaA), chrysene (Chry), benzo(*b*)fluoranthene (BbF), benzo(*k*)fluoranthene (BkF), benzo(a)pyrene (BaP), benzo(*e*)pyrene (BeP), indeno(1,2,3-*cd*)pyrene (IP), dibenz(*ah*)anthracene (DBahA) and benzo(*ghi*)perylene (BghiP).

4. Results and discussion

The wintertime sampling period included six pollution episodes, that is, when the PM10 concentrations of the day show increasing values that could be over the normative concentration (150 μg m^{-3}) the next day. The Mayor of Santiago decrees pollution episodes based on the information provided by the National Environmental Centre (CENMA) who receives and processes the PM10 concentration together with meteorological conditions (provided by SESMA and CENMA, respectively) according to an Air Quality model.

Table 1 reports the mean PM10 concentrations and ranges (minimum and maximum values) at Providencia and Las Condes in winter (under pollution episode conditions) and in spring, 2000.

Table 1 exhibits higher concentrations of PM10 during winter than during spring at both sampling sites; it also shows higher concentrations at Providencia than at Las Condes. On the other hand, our results show a decrease in PM10 concentrations in relation to those reported by Didyk et al. (2000) (250±88 μg m^{-3}) for June–July 1991, in a sampling site

Table 1

Mean and range of PM10 concentrations ($\mu g\ m^{-3}$) collected in winter and in spring, 2000, at Providencia and Las Condes

Sampling site	Number of samples	Sampling season	Mean PM10 concentration ($\mu g\ m^{-3}$)	Range PM10 concentration ($\mu g\ m^{-3}$)
Providencia	7	Winter (July 2000)	129.4±28.1	100.1–173.0
Las Condes	8	Winter (July 2000)	78.4±25.4	22.1–100.3
Providencia	9	Spring (September–October 2000)	64.2±17.1	31.6–89.9
Las Condes	9	Spring (September–October 2000)	57.9±17.2	29.1–84.9

located downtown about 1700 m west of Providencia. Such differences could be explained by the features of the various sampling sites, by the effects of the obligatory use of catalytic converters in new vehicles, and by the increasing restrictions to emissions of public transportation, since September 1992. These considerations agree with SESMA that reports decreasing concentrations of PM10 since 1998 (web page SESMA).

Tables 2 and 3 show mean, minimum and maximum concentrations for each PAH in PM10 at Providencia and Las Condes, respectively. The research of potential loss of PAHs on filters during collection was beyond the scope of this work. Such loss can be considered negligible for most of the quantified PAHs under the selected sampling conditions (Caricchia et al., 1999). Based on the facts mentioned above, concentrations given in Tables 2 and 3 become a good estimation of the environmental levels, except for the most

Table 2

Mean, minimum and maximum PAHs concentrations ($ng\ m^{-3}$) in PM10, at Providencia, year 2000

PAHs	Providencia					
	Winter concentration, $ng\ m^{-3}$			Spring concentration, $ng\ m^{-3}$		
	Mean	Minimum	Maximum	Mean	Minimum	Maximum
Ace	0.004	UDL[a]	0.010	UDL[a]	UDL[a]	0.003
Acy	0.061	0.024	0.117	0.016	UDL[a]	0.027
Flu	0.040	UDL[a]	0.066	0.016	UDL[a]	0.023
Nap	0.19	0.03	0.33	0.08	0.02	0.12
BaP	5.28	2.58	9.49	0.93	0.32	1.47
BeP	6.37	2.60	11.55	1.84	0.75	3.42
BbF	2.97	1.45	5.03	0.57	0.20	0.87
BkF	1.77	0.90	3.27	0.35	0.14	0.52
BghiP	3.82	2.15	5.96	0.96	0.35	1.52
DbahA	0.27	UDL[a]	0.71	0.05	UDL[a]	0.09
IP	2.48	0.87	4.62	0.56	0.22	0.86
Ant	0.18	0.08	0.31	0.05	0.03	0.07
Phe	1.07	0.46	1.75	0.30	0.05	0.42
Py	1.91	0.38	4.28	0.44	0.23	0.62
Fl	1.65	0.35	3.69	0.37	0.20	0.49
BaA	2.77	1.13	5.19	0.47	0.24	0.68
Chry	2.88	1.49	5.54	0.59	0.29	0.73
Total PAHs	33.73	13.93	59.98	7.61	2.97	11.58

[a] UDL: under detection limit.

Table 3
Mean, minimum and maximum PAHs concentrations (ng m^{-3}) in PM10, at Las Condes, year 2000

PAHs	Las Condes					
	Winter concentration, ng m^{-3}			Spring concentration, ng m^{-3}		
	Mean	Minimum	Maximum	Mean	Minimum	Maximum
Ace	0.003	UDL[a]	0.006	UDL[a]	UDL[a]	0.003
Acy	0.027	0.009	0.047	0.006	UDL[a]	0.012
Flu	0.022	0.011	0.033	0.007	UDL[a]	0.014
Nap	0.084	0.011	0.145	0.047	0.011	0.086
BaP	2.63	0.63	4.44	0.48	0.19	0.61
BeP	3.48	1.46	5.53	0.81	0.31	1.06
BbF	1.69	0.52	2.94	0.40	0.18	0.57
BkF	1.07	0.36	1.69	0.25	0.10	0.36
BghiP	1.52	0.42	2.83	0.42	0.19	0.54
DbahA	0.19	0.03	0.43	0.04	UDL[a]	0.06
IP	1.04	0.27	1.46	0.34	UDL[a]	0.52
Ant	0.07	0.03	0.12	0.03	0.02	0.04
Phe	0.50	0.19	0.79	0.18	0.07	0.28
Py	0.85	0.27	1.52	0.22	0.07	0.39
Fl	0.79	0.21	1.40	0.20	0.07	0.35
BaA	1.28	0.36	2.27	0.21	0.07	0.38
Chry	1.59	0.52	2.66	0.29	0.11	0.39
Total PAHs	16.86	5.32	28.31	3.94	1.39	5.67

[a] UDL: under detection limit.

volatile PAHs such as Nap, Acy, Ace, and Flu. Nevertheless, they are included in all the tables as they provide useful information.

Concentrations of individual compounds are in the range from under the detection limit to 11.6 ng m^{-3} depending on the sampling site and season of the year. The total PAHs concentration found is 14.2 ng m^{-3}, against 729 ng m^{-3} reported in 1991 (downtown) by Didyk et al. (2000). The remarkable differences between both studies (5 to 58 times) cannot be attributed to methodological differences, i.e. volatilization loss, which could only produced discrepancies of 100% and only for the more volatile PAHs, but to the effects of the reduction strategy of emissions implemented by the environmental authority (PPDA, 1997).

Tables 2 and 3 also show that total PAHs concentrations in winter are higher than those in spring (average factor of 4.4), and that total PAHs concentrations are approximately twice higher in Providencia than in Las Condes in both winter and spring.

The most abundant quantified PAHs in decreasing order are: BeP, BaP, BbF, Chry, BaA, BkF, DbaA, BghiP, IP in winter, and: BeP, BaP, BghiP, IP, BbF, Chry, BaA in spring. Benzofluoranthenes, benzopyrenes and chrysene, abundant in the analyzed samples, have been associated with combustion sources. Figs. 2 and 3 show daily concentrations of benzo(*a*)pyrene, benzo(*e*)pyrene, benzo(*b+k*)fluoranthene, benzo(*ghi*)perylene and chrysene in Providencia and in Las Condes sampling sites, during winter and spring, respectively. These PAHs were selected in accordance with two criteria: their classification as "probably" or "possibly" carcinogenic to humans by IARC (1987) and their higher concentrations.
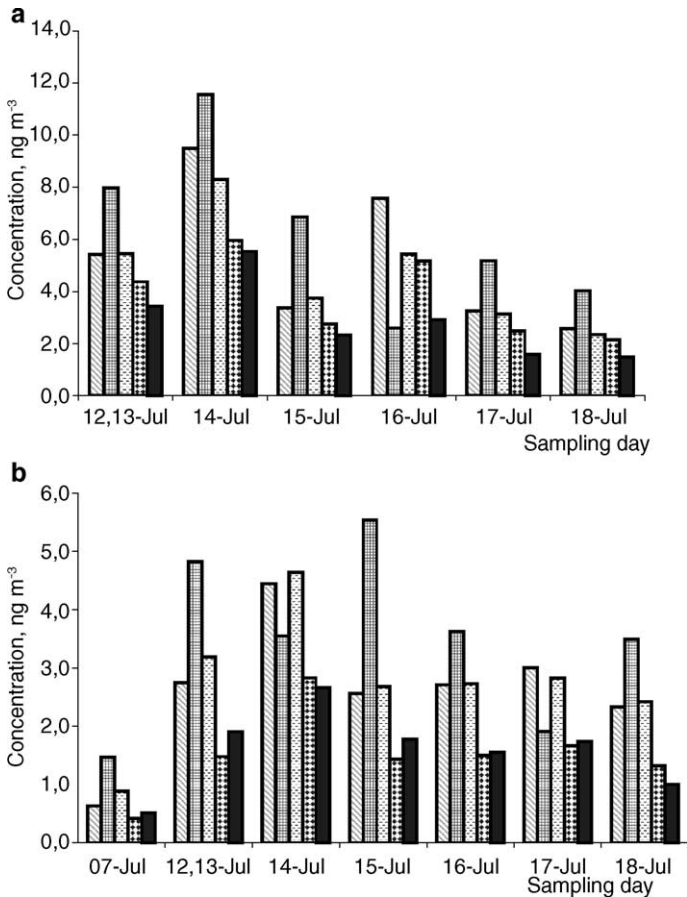
Fig. 2. Daily winter concentrations, year 2000, of ▨ benzo(*a*)pyrene, ▣ benzo(*e*)pyrene, ▦ benzo(*b+k*)fluoranthene, ⬕ benzo(*ghi*)perylene and ■ chrysene. (a) In Providencia and (b) in Las Condes sampling sites. Jul: July.

Figs. 2 and 3 also show that these PAHs concentrations in Providencia are higher than Las Condes in winter and in spring.

Daily levels of BaP, the most investigated PAH and often used as an indicator of total PAHs, are in the range of $0.63–9.49$ ng m^{-3} in winter and $0.19–1.47$ ng m^{-3} in spring. The average levels of BaP over the two sampling sites in the two campaigns were 5.28 and 0.90 in winter and spring respectively in Providencia; and 2.63 and 0.48 ng m^{-3} in winter and spring respectively at the Las Condes site. In Chile there is no regulation about PAHs but if we compare these values with the annual average value of 1 ng m^{-3} that the Italian regulation indicates as a quality objective, we can see that BaP levels exceed this limit during winter.

Table 4 shows total PAHs concentrations found in Santiago de Chile are similar to those found in other cities worlwide, like Kuala Lumpur (Omar et al., 2002), Naples (Caricchia et al., 1999) and Mumbai (Kulkarni and Venkataraman, 2000).
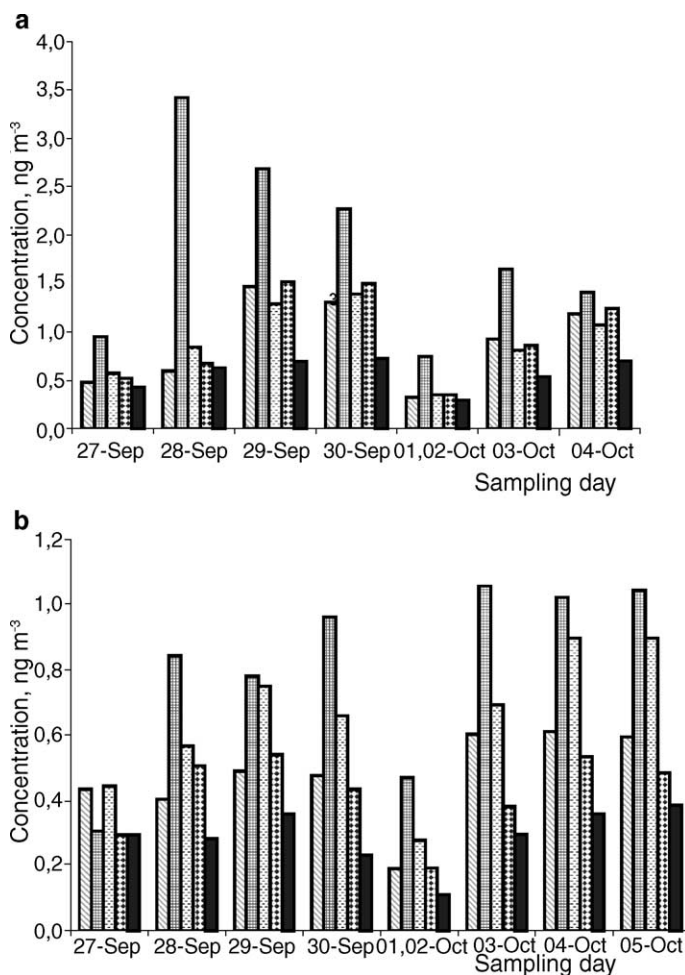
Fig. 3. Daily spring concentrations, year 2000, of ⬔ benzo(*a*)pyrene, ▨ benzo(*e*)pyrene, ▥ benzo(*b+k*)fluoranthene, ⬓ benzo(*ghi*)perylene and ▪ chrysene. (a) In Providencia and (b) in las Condes sampling sites. Sep: September, Oct: October.

Considering that PAHs have their highest concentrations in the respirable size of airborne particulate matter, our results show a considerable decrease in the PAHs concentrations with time. The percentage of carcinogenic PAHs (BaA+BaP+DBahA+IP+BkF+BbF+Chry) related to total PAHs were 54.6% at Providencia and 56.3% at Las Condes during July and 46.5% at Providencia and 51.0% at Las Condes during spring. These concentrations denote the possible harmful incidence on human health of this particulate matter.

Table 5 shows the cold/hot ratio mean concentrations (corresponding to ratio winter/spring concentrations, 7.5/14.7 mean temperatures) for individual PAHs ranging from 0.5 to 12.6 with an average of 5.2 in Providencia, and from 1.8 to 9.1 with an average of 4.3 in Las Condes.

Table 4
Ranges for total PAHs concentrations in PM10 quantified worldwide

Site of study	Total PAHs concentration (ng m^{-3})	Particles diameter	Sampling time (h)	Reference
Naples, Italy 1996–1997	2–130	PM10	24	Caricchia et al., 1999
Mumbai, India, urban	24.5 at Saki Naka 38.8 at Indian Institute of Technology	PM10	72	Kulkarni and Venkataraman, 2000
Kuala Lumpur, Malaysia, urban, November 1998–January 1999	6.28±4.35	PM10	24	Omar et al., 2002
Santiago, July 2000	5.45–61.93	PM10	24	This study
Santiago, September–October 2000	1.79–10.91	PM10	24	This study

Cold/hot ratios show a higher variability for PAHs in smaller concentrations like Ace, Acy, Nap and Flu, which are also the more volatile compounds. The relative proportions of individual compounds differ significantly in cold and hot seasons, possibly reflecting changes in PAHs emissions sources and/or atmospheric conditions. The higher concentrations of PAHs during the cold season might be principally related to various factors: the different vapor pressures of PAHs at ambient temperature, the height of the inversion limit layer, which in winter is lower than in spring and slow contaminants dispersion, the increased emissions from burning of fossil fuels for domestic heating and other factors that can cause chemical and photochemical degradation of some PAHs.

The concentrations of some marker compounds and their ratios can give some indication about the impact of different sources of airborne compounds (Pistikopoulos et al., 1990; Pio et al., 2001). This matter is still widely debated. These marker compounds

Table 5
Cold/hot ratio mean concentrations for PAHs in PM10 collected at two sites of Santiago (Providencia and Las Condes), 2000

PAHs	Providencia cold/hot ratio	Las Condes cold/hot ratio
Acenaphthene	12.59	9.06
Acenaphthylene	3.76	4.35
Fluorene	0.51	2.96
Naphthalene	11.59	1.78
Benzo(*a*)pyrene	5.65	5.52
Benzo(*e*)pyrene	3.45	4.29
Benzo(*b*)fluoranthene	5.18	4.21
Benzo(*k*)fluoranthene	5.00	4.34
Benzo(*ghi*)perylene	3.97	3.60
Dibenz(*a*,*h*)anthracene	4.85	4.70
Indeno(1,2,3-*cd*)pyrene	4.43	3.07
Anthracene	3.54	2.20
Phenanthrene	3.63	2.87
Pyrene	4.32	3.81
Fluoranthene	4.53	3.89
Benzo(*a*)anthracene	5.90	6.05
Chrysene	4.86	5.48

are often used to indicate the prevalence of gasoline or diesel engines as well as the relative contribution of traffic, domestic heating, wood combustion and other sources. For this purpose, some molecular diagnostic ratios can be used, e.g. CPAH/TPAH, IP/(IP+BghiP), Phe/(Phe+Ant), BaA/(BaA+Chry), Fl/(Fl+Py) and BeP/(BeP+BaP).

The sum of the concentrations of the nine following combustion PAHs (CPAH): Fl, Py, BaA, BbF, BkF, BaP, BeP, IP and BghiP divided by the total concentration of the PAHs (TPAH) has often been used as a characteristic diagnostic parameter for PAHs produced by stationary combustion sources. Rogge et al. (1993a) determined the value of CPAH/TPAH ratio for non-catalyst (0.41) and catalyst-equipped (0.51) automobiles and for heavy-duty diesel trucks (0.30). The results of this study show a CPAH/TPAH in Santiago of 0.72 ± 0.02 in winter and 0.71 ± 0.05 in spring. After correcting the concentrations of Fl, Py, Ant and Phe by their percentage of volatilization loss given by Kavouras et al. (1999), the mean value for the CPAH/TPAH ratio is changed to 0.60 ± 0.05. This value denotes that a considerable portion of PAHs mass could originate from combustion from mobile sources such as catalyst-equipped automobiles.

The average value of IP/(IP+BghiP) ratio obtained in this work was 0.40 ± 0.13 for winter and 0.40 ± 0.11 for spring. Values previously documented of 0.18 for gasoline emissions (Kavouras et al., 1999; Pio et al., 2001, Alves et al., 2001; Cereceda-Balic et al., 2002), 0.37–0.70 for diesel emissions (Kavouras et al., 1999, 2001; Pio et al., 2001, Alves et al., 2001; Cereceda-Balic et al., 2002), 0.56 for coal powder (Pio et al., 2001) and 0.62 for wood combustion emissions (Gogou et al., 1996), denote the importance of diesel emissions in the study sites.

BaA/(BaA+Chry) ratio is generally used to evaluate the contribution of vehicular emissions. The mean value of this ratio for Santiago was 0.46 ± 0.04 in winter and 0.43 ± 0.05 in spring. Values for this ratio reported in the literature are: 0.16 for rural samples, 0.33 for urban samples with catalyst-equipped vehicles (Gogou et al., 1996), 0.50 for industrial and heavy-truck emissions, 0.38–0.65 for diesel motors, 0.43 for gasoline motors (Kavouras et al., 2001). This information could indicate the importance of gasoline and diesel engine emissions to Santiago's atmosphere.

The mean value of Fl/(Fl+Py) ratio obtained in this work was 0.47 ± 0.03 in winter and in spring. This value was similar to those previously documented for automobile emissions, particularly catalyst-equipped automobiles by Kavouras et al. (1999) for Santiago and by Rogge et al. (1993b).

The diagnostic ratio Phe/(Phe+Ant) has been used to identify the importance of petrogenic hydrocarbons in relation to emissions from biomass burning. Values of this ratio higher than 0.7 are typically associated with lubricant oils and fossil fuels (Alves et al., 2001). The mean values obtained in this study (0.87 ± 0.02 in winter and 0.85 ± 0.08 in spring) denote the significance of phenanthrene derived from lubricant oils and burning fossil fuels in Santiago.

The average value of the BeP/(BeP+BaP) ratio was 0.56 ± 0.13 in winter and 0.63 ± 0.09 in spring. These values were similar to those documented for diesel vehicles reported by Sicre et al. (1987) and by Simcik et al. (1999); 0.53 ± 0.05 and 0.4–0.5, respectively. They reflect the significance of diesel emissions.

Concentration ratios of PAHs relative to both BaP and BeP are summarized in Table 6, with the season's means and ranges. The ratios to BaP for BFA were the highest with a

Table 6
Summary of PAH profiles relative to BaP and BeP

Season		Ratios of each PAH relative to BaP				Ratios of each PAH relative to BeP			
		BaA	BFA	IP	DBahA	BaA	BFA	IP	DBahA
Providencia July 2000	Mean	0.51	0.93	0.47	0.05	0.54	0.87	0.53	0.05
	Range	0.39–0.57	0.71–1.11	0.16–0.59	0.00–0.07	0.25–1.59	0.55–2.08	0.11–1.72	0.00–0.11
	S.D.	0.07	0.13	0.16	0.03	0.52	0.60	0.59	0.04
	CV (%)	14	14	33	59	98	67	112	82
Las Condes July 2000	Mean	0.49	1.09	0.44	0.07	0.40	0.86	0.33	0.06
	Range	0.36–0.57	0.94–1.39	0.06–0.56	0.05–0.10	0.24–0.76	0.48–1.48	0.08–0.77	0.02–0.08
	S.D.	0.07	0.15	0.17	0.02	0.21	0.38	0.22	0.03
	CV (%)	14	14	39	26	54	45	66	61
Providencia September– October 2000	Mean	0.54	1.04	0.63	0.05	0.28	0.54	0.34	0.03
	Range	0.33–0.75	0.88–1.41	0.48–0.76	0.00–0.08	0.13–0.44	0.25–0.76	0.12–0.54	0.00–0.06
	S.D.	0.14	0.19	0.09	0.03	0.10	0.16	0.12	0.02
	CV (%)	25	18	14	51	35	29	36	58
Las Condes September– October 2000	Mean	0.43	1.36	0.72	0.08	0.28	0.84	0.38	0.04
	Range	0.35–0.64	1.02–1.53	0.00–0.99	0.00–0.12	0.15–0.37	0.59–1.44	0.00–0.50	0.00–0.06
	S.D.	0.11	0.18	0.31	0.04	0.16	0.28	0.16	0.02
	CV (%)	24	13	43	47	56	33	42	46

BFA: Sum of BbF and BkF.

coefficient of variation between 13% and 18%. BbF and BkF are two of the relatively stable PAHs. For BFA and IP the highest values of the ratios to BaP were measured in September–October, which are the months with the maximum number of daylight hours, the maximum sunlight intensity and the highest ozone concentrations (as measured in the monitoring network). This provides indirect evidence of the important contribution of photodegradation to the decay of adsorbed BaP as shown under simulated experimental conditions (Lane, 1989). The ratios of DBahA relative both to BaP and to BeP showed no seasonality but variability.

5. Conclusions

Total PAHs concentrations ranges were 5.45–61.93 ng m^{-3} in winter and 1.79–10.91 ng m^{-3} in spring. Concentration levels of PAHs observed during 2000 are significantly lower than previous studies, but they are still high enough, in particular for carcinogenic PAHs indicating an exposure of the inhabitants of Santiago to high amount of carcinogenic/mutagenic air pollutants.

The mean values of CPAH/TPAH, BaA/(BaA+Chry), Fl/(Fl+Py), Phe/(Phe+Ant), BeP/(BeP+BaP) and IP/(IP+BghiP) ratios are indicators of emissions coming from non-catalyst, catalyst-equipped automobiles and heavy-duty-diesel trucks. Vehicular emissions were the major source of PM10 in Santiago during the sampling period.

BaP and other carcinogenic PAHs concentrations are still a matter of concern. These results indicate the necessity of a continuous research in this field to control health consequences of these toxics on citizens' health.

The ratios of PAH relative to BaP and to its isomer BeP were consistent with the different PAH degradabilities, occurring at a higher rate under summer conditions.

Acknowledgements

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