

Sources, distribution and variability of airborne particles and hydrocarbons in La Plata area, Argentina

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Received 8 January 1998; accepted 24 July 1998

Abstract

Total suspended particles (TSP), particulate- (ALIp) and semi-volatile aliphatic hydrocarbons (ALIsv) were measured in air sampled during the day and night over 7–8 months in industrial, commercial and residential sectors of La Plata, Argentina. TSP, ALIp and ALIsv ranges were 23–219 $\mu\text{g}/\text{m}^3$, 11–447 and 12–719 ng/m^3 , respectively. Maximum values were recorded at a downtown site whereas the residential station showed lower levels. Concentrations were usually higher during the day and during fall and winter. Two- and three-way ANOVA were performed to evaluate the day-night, inter-station, and inter-month variability. The amount of total variability accounted by these factors was 14, 25 and 23% ($p < 0.01$) for TSP; 0.8, 11 and 39% ($p < 0.03$) for ALIp; and 0.6, 7.9 and 15% ($p < 0.3$) for ALIsv, respectively. Overall, the inter-month variability prevailed; inter-station differences were most significant in the summer when the day-night variability was lower. For the particulate phase, the day-night differences were more significant at the downtown and residential sites. The composition of ALIp and ALIsv reflected the contribution from biogenic long chain odd *n*-alkanes and petrogenic lower molecular weight *n*-alkanes. Plant cuticular waxes accounted for 34–96% of ALIp with higher values during the summer and at the Residential station. A principal component analysis clearly discriminated ALIsv, almost entirely derived from exhaust and diesel fuel emissions, from ALIp composed of mixed biogenic-petrogenic sources. The lowest day-night differences observed during the summer were related to a higher proportion of biogenic “natural” material during this period of full plant grow and lower vehicle circulation. The larger day-night differences registered at the downtown station were related to an enhanced input of anthropic sources (vehicles, fossil fuels, lubricating oils) during the most active day period. © 1999 Elsevier Science Ltd. All rights reserved.

Keywords: Airborne particles; Aliphatic hydrocarbons; Air quality; Argentina

1. Introduction

The urban atmosphere is subjected to large inputs of anthropogenic contaminants arising from both stationary (power plants, industries, commerce and residential heating) and mobile sources (transit and transportation). The composition of airborne hydrocarbons is usually complex reflecting the contribution of several sources: automobile exhaust, lubricating oils, gasoline, diesel fuel, tire particles, asphalt, weathered street material, biomass combustion, biogenic particles (Takada et al., 1990; Simoneit, 1984; Simoneit et al., 1993; Aboul-Kassim and Simoneit, 1995; Gogou et al.,

1996; Schauer et al., 1996.) According to their different physical and chemical properties (vapor pressure, Henry law constant), and the size and composition of the source particles, hydrocarbons partition between the particulate and vapor phases and are subsequently transported to the earth surface through dry and wet deposition (Webber, 1986; Simoneit and Mazurek, 1989; Dickhut and Gustafson, 1995; Poster and Baker, 1996a, 1996b). On a toxicological point of view, this airborne particulated material produces important adverse health effects, principally through the inhalation of fine ($\text{PM}_{2.5}$) particles (e.g. Dockery and Pope, 1994; Reichhardt, 1995; Great Lakes Center for Occupational and Environmental Safety and Health, 1997). The deleterious effect of the airborne material is aggravated by the coexistence of semi-volatile compounds of high mutagenicity potential (Westerholm et al., 1991). On a biogeo-

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chemical perspective, urban airborne material is an important source of anthropogenic compounds to the aquatic environment. After heavy rain events, the street dust containing very complex mixtures of hydrocarbons, trace metals and other xenobiotics is washed to their ultimate long-term reservoir: sediments from rivers, estuaries and coastal areas.

In this paper we report the results of a study of airborne particles, particulate (ALIp) and semi-volatile aliphatic hydrocarbons (ALIsv) sampled during day and night hours over 8 months at four stations located in industrial, commercial and residential sectors of La Plata city. These data permitted the evaluation of the sources, distribution and variability of the airborne material as well as the first characterization of the hydrocarbon composition of this urban aerosol which constitute an important diffuse source to the nearby Río de la Plata Estuary.

2. Materials and methods

2.1. Study area and sampling

The study area is centered around La Plata city, capital of Buenos Aires state, situated 15 km away from the Río de la Plata Estuary coast in the most industrialized and densely populated region of Argentina. It includes the nearby cities of Berisso and Ensenada and comprises a heavy petrochemical sector with the major oil refinery of the country and several associated industries, and a total population of about 1,000,000 people.

To identify the most important hydrocarbon sources, four sampling stations were established in a 25 km long NE-SW transect passing through the petrochemical area and La Plata city center (Fig. 1): La Plata port (Port), petrochemical sector (Petrochemical), La Plata city center (Downtown), and Etcheverry, a less urbanized

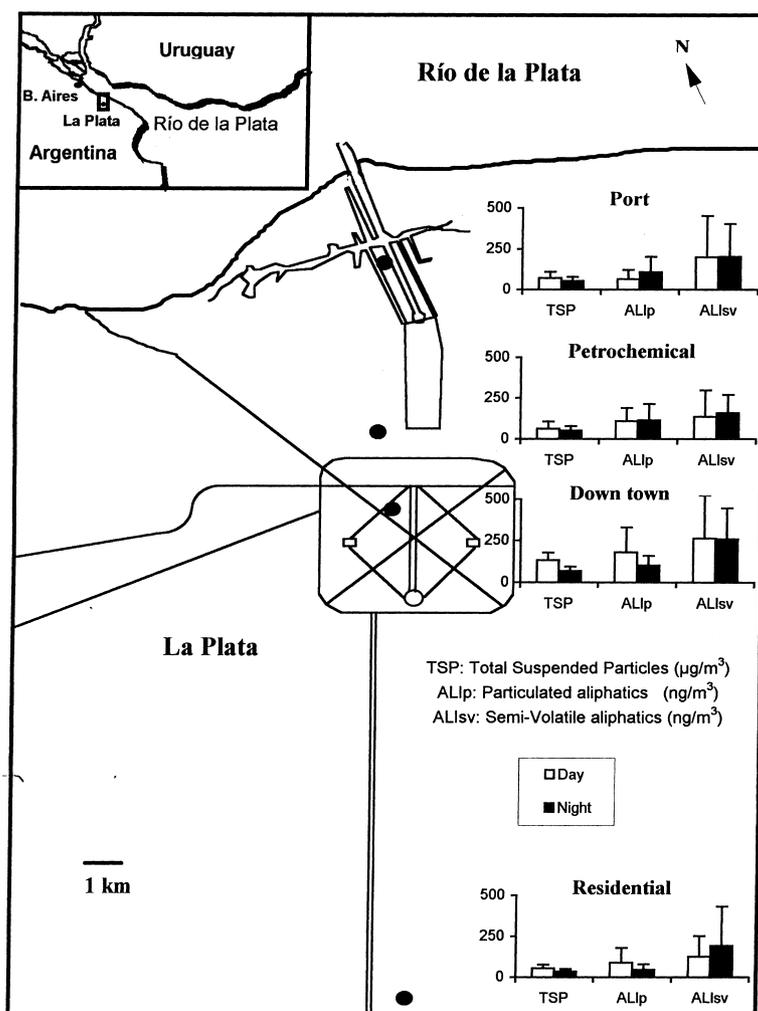


Fig. 1. Study area, station location and average day-night values for airborne TSP, ALIp and ALIsv. Major roads and central parks (open circles and rectangles) of La Plata city are indicated. Sampling stations are shown as filled circles.

Table 1—(Continued)

	TSP		ALIp		ALIsv		Composition of ALIp (%)										Composition of ALIsv (%)													
	($\mu\text{g}/\text{m}^3$)	D	(ng/m^3)	D	(ng/m^3)	D	$n\text{-C}_{21}$	$n\text{-C}_{22}$	$n\text{-C}_{23}$	$n\text{-C}_{24}$	$n\text{-C}_{25}$	$n\text{-C}_{26}$	$n\text{-C}_{27}$	$n\text{-C}_{28}$	$n\text{-C}_{29}$	$n\text{-C}_{30}$	$n\text{-C}_{31}$	Odd/Ev	L/H	$n\text{-C}_{19}$	$n\text{-C}_{20}$	$n\text{-C}_{24}$	$n\text{-C}_{25}$	Odd/Ev	Alk/Iso					
Down town	99	101	97	70	34	612	3.2	7.3	6.7	10.0	11.2	7.9	2.7	7.6	1.2	1.4	0.9	1.3	19.9	20.8	25.6	19.3	2.1	1.3	1.5	0.4	0.9	1.0	1.3	1.6
Residential	36	37	20	26	0.5	0.6	0.9	0.9	0.9	22.1	17.6	31.4	19.6	4.9	2.1	0.1	0.2													

TSP: total suspended particles; ALIp: total particulate aliphatics; ALIsv: total semi-volatile aliphatics; D: day; N: night; $n\text{-C}_{19}$ to $n\text{-C}_{31}$: n -alkanes with that chain length; Odd/Ev: odd/even n -alkanes; L/H: $< \text{C}_{25} / > \text{C}_{25}$ n -alkanes; Alk/Iso: $n\text{-C}_{17}$ + $n\text{-C}_{18}$ /Norpristane + Pristane + Phytane.

area 12 km away from La Plata (Residential). Sampling was carried out in 7–8 different months during the year 1993 (January–May, July, August and December) using two General Metals Works BM 2200X portable high volume samplers located ~6 m above the ground for security reasons. To establish day-night differences, samplers were operated in 2 discontinuous periods of 12 h, one during the day (9:00 AM to 9:00 PM) and the other during the night (9:00 PM to 9:00 AM). The total sampling period was about 48 h (24 h day and 24 h night) during which the samplers pumped in average $2170 \pm 500 \text{ m}^3$ of air. Due to electricity failures and incorrect operation of the sampling equipment, the data set is incomplete for some months and stations (specially for July and the residential site; Table 1). Meteorological data (average temperature, relative humidity and wind direction) were obtained for each sampling date from the Astronomy Observatory of La Plata city.

Suspended particles were collected on previously extracted (acetone–petroleum ether 1:2) and calcined (1 h at 450°C) Whatman EPM 2000 glass fiber filters (99.999% retention for $0.6 \mu\text{m}$ NaCl particles). Total suspended particle (TSP) weight was determined by gravimetry, drying (40°C to constant weight) and weighing the filters in glass tubes before and after sampling. Dried filters were cut in two equal halves and re-weighed, one half was used for hydrocarbon analysis and the other was separated for trace metal determinations. The filters were stored frozen (-20°C) until

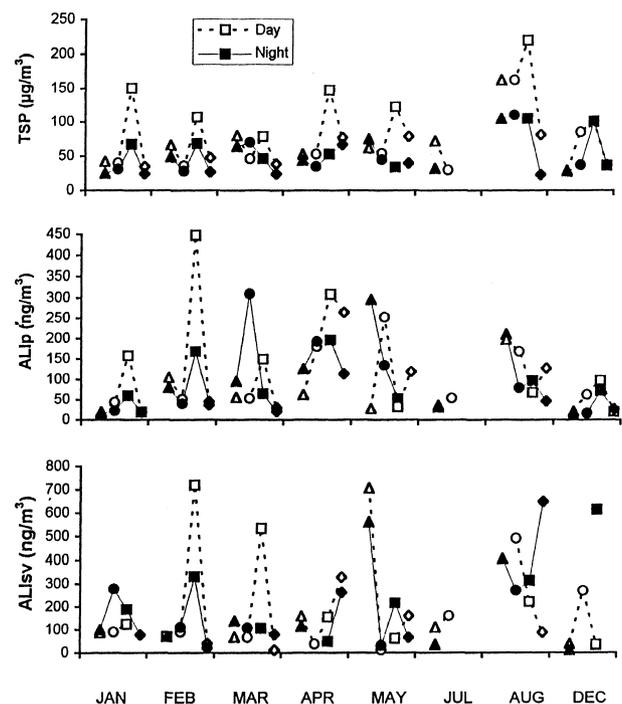


Fig. 2. Concentrations of TSP, ALIp and ALIsv in the day and night air samples at the four stations and eight sampling months. Stations are identified by triangles (Port), circles (Petrochemical), squares (Downtown) and diamonds (Residential).

extraction. ALIsv were collected on pre-washed (soap + deionized water) and pre-extracted (10 h Soxhlet with petroleum ether) $20 \times 25 \times 2$ cm polyurethane foam plugs (density: 23 mg/cm^3) placed directly below the glass fiber filters in a specially constructed frame.

2.2. Chemical analysis

ALIp were extracted with a 1:2 acetone–petroleum ether mixture and sonication. The filters were treated 4 times (10 min each) with a total solvent volume of 100 ml. ALIsv adsorbed on the polyurethane foams were Soxhlet extracted with petroleum ether (10 h). The extracts were concentrated and subsequently purified on silica gel microcolumns (1 g of 3% deactivated adsorbent) eluted with petroleum ether. Separation of the individual aliphatic components (*n*-alkanes and isoprenoids) was carried out by high-resolution gas chromatography using a Shimadzu GC-7AG gas chromatograph equipped with a $0.25 \text{ mm} \times 30 \text{ m}$ SPB-5 silica column, a split-splitless injector and a flame ionization detector operated at 320°C . The column temperature was programmed from 135 (1 min hold) to 295°C (8 min hold) at $3.5^\circ\text{C}/\text{min}$. Procedural blanks and authentic aliphatic hydrocarbon standards (Supelco) were run periodically, once each 5–10 samples. Quantification was carried out by calculation of individual response factors which typically varied by $\pm 10\%$ in the different runs. The recovery yield of spiked filters averaged 93% for C_{15} to C_{35} *n*-alkanes. The reproducibility of the analyses ranged from 8 to 25% (RSD).

3. Results and discussion

3.1. Total suspended particle and hydrocarbon concentrations

Table 1 presents the total concentrations of suspended particles, and of ALIp and ALIsv as well as their relative composition in the day and night air samples. TSP concentrations ranged from 23 to $219 \mu\text{g}/\text{m}^3$; total particulate and semi-volatile aliphatic levels oscillated from 11 to 447 and from 12 to $719 \text{ ng}/\text{m}^3$, respectively. Maximum values of all three parameters were recorded during the day at the downtown station whereas the residential site generally showed the lowest levels. The average values of TSP, ALIp and ALIsv for each station are compared in Fig. 1. The downtown site shows the highest concentrations. The averages (\pm standard deviation) at this station are: $100 \pm 49 \mu\text{g TSP}/\text{m}^3$, $140 \pm 115 \text{ ng ALIp}/\text{m}^3$ and $261 \pm 218 \text{ ng ALIsv}/\text{m}^3$, compared to 62 ± 35 , 50 ± 22 , $59 \pm 37 \mu\text{g TSP}/\text{m}^3$; 94 ± 87 , 115 ± 93 , $68 \pm 72 \text{ ng ALIp}/\text{m}^3$ and 178 ± 209 , 155 ± 137 , $162 \pm 190 \text{ ng ALIsv}/\text{m}^3$ for the Port, Petrochemical, and Residential stations, respec-

tively. These higher averages registered at the downtown place reflect the importance of mobile sources (vehicles) in the most important commercial sector of the city which also shows a dominant contribution of petrogenic hydrocarbons (see composition section). The higher values observed during the most active day-period (Fig. 1) support this interpretation (see variability section).

The annual-average of $100 \mu\text{g TSP}/\text{m}^3$ measured at the downtown site is below the national regulation of $150 \mu\text{g}/\text{m}^3$ but is higher than the World Health Organization recommended values of 60–90 $\mu\text{g}/\text{m}^3$. This annual-average TSP value at La Plata downtown site is in the middle-range of values reported for world cities (> 300 – $400 \mu\text{g}/\text{m}^3$ at New Delhi and Calcutta) but is higher than those of clean industrialized cities (30–55 $\mu\text{g TSP}/\text{m}^3$ at Frankfurt, Copenhagen and 14 Canadian cities; Great Lakes Center for Occupational and Environmental Safety and Health, 1997). The hydrocarbon averages at our most polluted downtown place (140–261 ng/m^3) are comparable to the values reported for other urban areas, 76–316 ng/m^3 in eastern Mediterranean cities, 198–314 ng/m^3 in Barcelona and 20–146 ng/m^3 in Los Angeles (Gogou et al., 1996).

The concentrations of aliphatic hydrocarbons in TSP on a dry weight basis are relatively high (day vs night): 850 ± 390 vs $1740 \pm 1120 \mu\text{g}/\text{g}$ at the Port, 1900 ± 1380 vs. $2300 \pm 1980 \mu\text{g}/\text{g}$ at Petrochemical, 1540 ± 1380 vs. $1650 \pm 1070 \mu\text{g}/\text{g}$ at the Downtown and 1320 ± 1030 vs. $1280 \pm 560 \mu\text{g}/\text{g}$ at the Residential sites. The lower values generally observed during the day probably reflect the dilution produced by resuspension of larger particles (dust) with lower hydrocarbon levels and enriched in plant material (see hydrocarbon composition) during the day. This dust resuspension is favored by the higher temperatures ($24 \pm 3.1^\circ\text{C}$ in summer and $13 \pm 2.2^\circ\text{C}$ in winter), lower humidity ($69 \pm 8.2\%$ and $66 \pm 16\%$) and higher human activity during the day relative to the night (20 ± 3.5 and $8.7 \pm 8.8^\circ\text{C}$; 84 ± 6.5 and $88 \pm 11\%$, respectively), when smaller, hydrocarbon-enriched particles would predominate. The concentrations of *n*-alkanes in TSP collected in La Plata area are comparable to those reported for other world cities: 60–937 $\mu\text{g}/\text{g}$ in Alexandria, Egypt, 850–3570 $\mu\text{g}/\text{g}$ in Eastern Mediterranean cities (Aboul-Kassim and Simoneit, 1995; Gogou et al., 1996).

3.2. Diurnal, inter-station and inter-month variability

All three variables measured in air from La Plata region show considerable variability (Table 1). As observed in Fig. 1, particulate concentrations are generally higher during the day (24–94% higher for TSP), especially at the downtown site. However, the inter-station and inter-month variability are also very important (Fig. 2). The concentrations of TSP, ALIp and ALIsv

generally increase from January–April, May, August and decrease in December. To evaluate the different contribution of these three sources of variability (day-night, inter-station, and inter-month) we performed two- and three-way ANOVA for the log-transformed data (July was excluded due to the paucity of data.) In a first step, we examined the evolution of the day-night and inter-station differences by month with two-way ANOVA. For TSP, the inter-station differences explained on average 64% of the total variability, with the highest values in January, February (78%, $p < 0.01$) and December (84%, $p = 0.07$). The day-night differences explained 4–47% of the total variability, with low values during the summer (January, February, December), the maximum in May ($p = 0.9$) and an average of 24%. This lower incidence of the day-night differences during summer months is probably related to the reduced general activity and subsequent lower vehicle circulation during the holiday period. Basically the same pattern is observed for particulate aliphatics; the inter-station differences explained in average 66% of the total variability, with highest values in the summer (72–89%, $p = 0.12 - 0.03$). The day-night differences averaged only 6.5% in this case. For ALIsv, the inter-station differences averaged 63% of the total variability and presented higher values in February (94%; $p = 0.01$) and May (88%; $p = 0.06$). The day-night differences averaged 14% peaking in January (21%; $p = 0.22$) and August (39%; $p = 0.15$). These results indicate more variable trends, independent from the behavior of the particulate phase, for the ALIsv.

In a second step, the day-night and inter-month (temporal) trends were evaluated for each station separately with two-way ANOVA. For TSP, the inter-month differences accounted in average for 60% of the total variability, with higher values at the Port and Petrochemical stations (80–83%; $p < 0.02$) and lower percentages at the Downtown and Residential sites (35–45%, $p < 0.2$). Conversely, the day-night differences were most significant ($p < 0.02$) at the Downtown (49%) and Residential (36%) sites, and very low at the Port and Petrochemical stations (8–12%) with a general average of 32%. These results indicate more constant month to month TSP inputs and comparatively larger day-night differences at the Downtown and Residential sites. For ALIp, the inter-month differences averaged 67% of the total variability and were more homogeneous in the four stations (46–76%). The higher values corresponded to the Downtown and Port sites (75–76%, $p = 0.07 - 0.04$), whereas the day-night differences explained a low amount of the total variance (6.5%). The inter-month differences were also predominant for ALIsv accounting for 54% of the total variability with the highest value at the Downtown (87%; $p = 0.01$) site. The day-night differences were very low (4% total variability) in this case.

A final, general analysis of the three sources of variability was carried out by a three-factor (day-night, inter-station and inter-month) ANOVA. The amount of the total variability explained by the day-night, inter-station and inter-month differences were: 14, 25 and 23% for TSP ($p < 0.01$ for all); 0.8 ($p = 0.40$), 11 ($p = 0.02$) and 39% ($p < 0.01$) for ALIp; and 0.6 ($p = 0.58$), 7.9 ($p = 0.28$) and 15% ($p = 0.30$) for ALIsv. These results indicate that overall, taking the four stations and all the sampling months together, the inter-month (temporal) trend is usually the most significant, comparable to the inter-station differences in the case of TSP. The first two-way ANOVAs indicated that the day-night (vs. inter-station) differences were comparatively more important during fall and winter months and at the Downtown and Residential stations (vs. the inter-month variability for TSP). The trends observed did not show any significant covariation with meteorological data. The sole exception is a weak positive correlation ($r = 0.41 - 0.47$) of TSP and ALIp with wind direction during the night: the concentrations increase with winds blowing from the third and fourth quadrants (S-W, W, N-W), i.e. from the continent not from the Río de la Plata. No significant trend is observed for the day samples nor for Temperature-TSP, ALIp and ALIsv relationships, possibly reflecting the overwhelming influence of the mobile source emission pattern (see composition section).

3.3. Composition of particulate and semi-volatile airborne hydrocarbons

Fig. 3 presents the percent composition of airborne hydrocarbons. Particulate hydrocarbons consist of *n*-alkanes ranging from 17 to 32 carbons and show clearly distinct patterns in January and May. A strong contribution of high molecular weight odd *n*-alkanes (C_{29} and C_{31}) over a smooth general trend maximizing at C_{25-26} is observed in January, whereas a higher relative abundance of lower molecular weight *n*-alkanes peaking at C_{22-23} and a reduction of the odd carbon signal is detected in May.

The high molecular weight odd *n*-alkanes are characteristic of cuticular waxes from vascular plants (Colombo et al., 1989) and have been identified as major components of aerosols collected in urban and rural areas (Simoneit, 1989; Simoneit et al., 1990; Simoneit et al., 1991; Gogou et al., 1996). Leaves from *Fraxinus* sp, a widespread tree in La Plata region, have been analyzed in the four sampling stations yielding a strong odd carbon predominance (33 and 21% of total aliphatics for *n*- C_{29} and *n*- C_{31} , Colombo, 1997 unpublished results), very similar to the values registered at the Residential site during summer months (January, February, December, Table 1). An estimation of the contribution of vascular plant material to the airborne

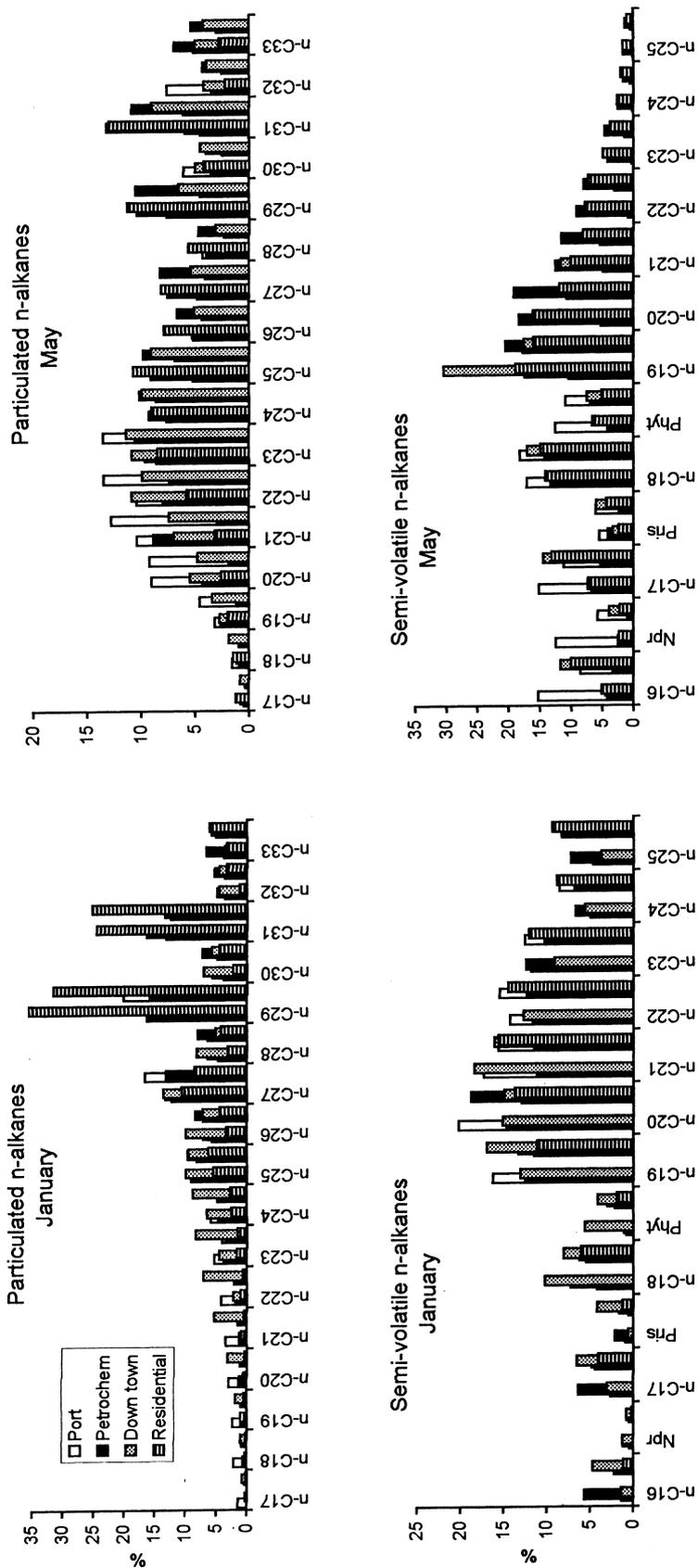


Fig. 3. Relative composition of ALIp and ALIsv in the four stations in January (summer) and May (fall).

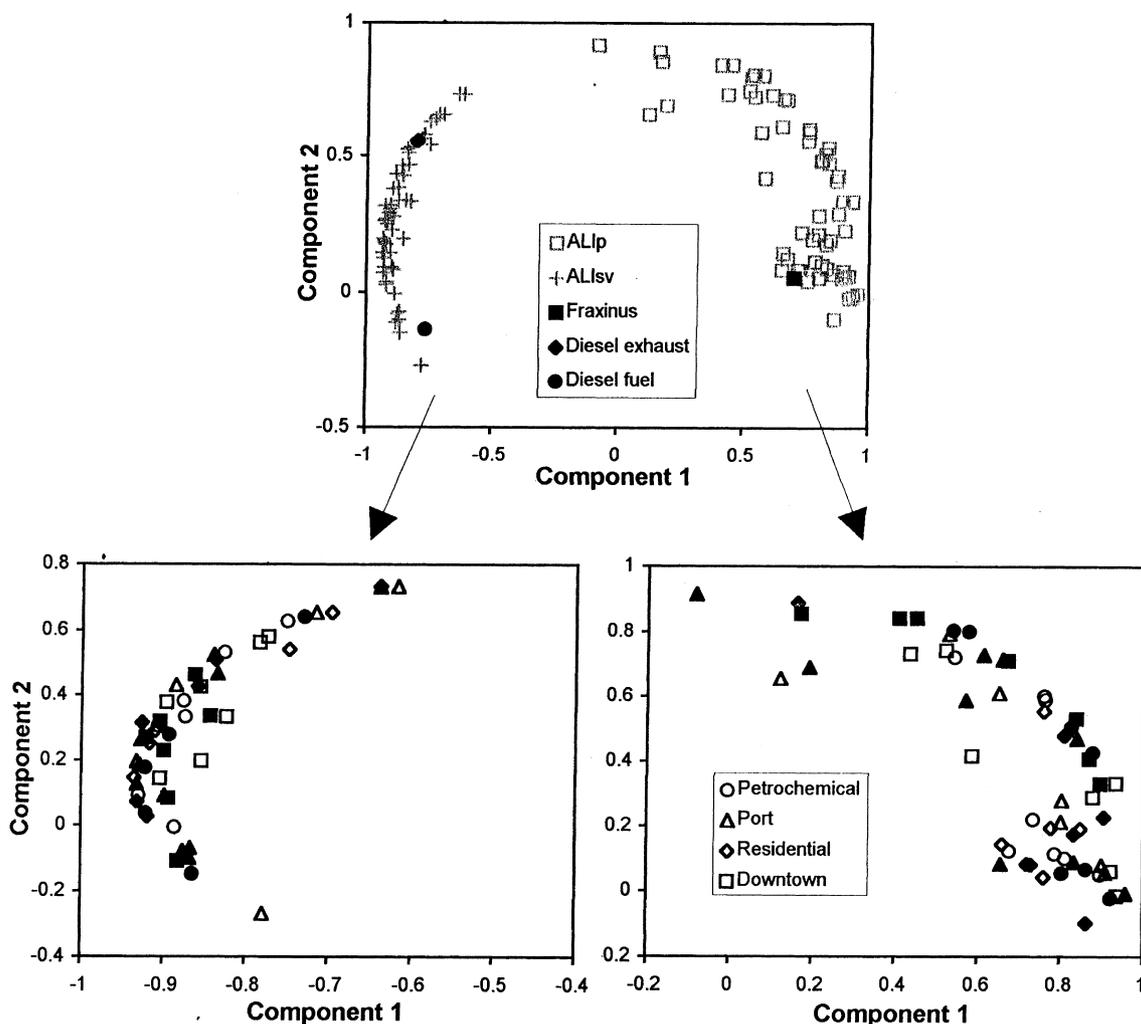


Fig. 4. Principal component analysis performed with the correlation matrix of the relative hydrocarbon composition of semi-volatile and particulated samples. The *n*-alkane composition of a local tree (*Fraxinus* sp), a local diesel fuel and that reported for diesel exhausts (Simoneit, 1986) are also included. The sample codes are the same as Fig. 2.

hydrocarbons was obtained considering the relative contribution of *n*-alkanes of chain length higher than C_{27} in *Fraxinus* leaves (89% total aliphatics, considered as 100% contribution of plant material) and in the ALIp samples. These calculations indicated that plant material contributes 34–96% of the airborne particulate aliphatic hydrocarbons. The values are higher in the Petrochemical and Residential stations (global average $\approx 60\%$) and lower at the Downtown site (47%) with a 8–30% increase during the day period. The background signal of lower molecular weight *n*-alkanes represent the contribution of unburned hydrocarbons from mobile sources and is more apparent at the Downtown station.

ALIsv analyzed consist of *n*-alkanes from C_{16} to C_{25} plus the isoprenoids norpristane, pristane and phytane. The composition of this semi-volatile fraction is consistent with the particulate phase trend: in January, the series maximize at C_{20} and show a relatively elevated proportion of higher molecular weight compounds,

whereas in May there is a stronger contribution of more volatile compounds maximizing at C_{19} with minor proportions of $> C_{23}$ *n*-alkanes. This shift to lower molecular weight *n*-alkanes reflects a higher relative contribution from mobile sources (fossil fuels) in May, and specially at the Downtown site.

The study of molecular markers in vehicular exhausts and source materials (Simoneit, 1985) indicated that the aliphatic signal of diesel and gasoline engines consist of a narrow band of C_{15-27} *n*-alkanes maximizing at C_{20-21} , very similar to the pattern of lubricating oils (n - C_{13-27} maximizing at C_{19}). The signal of diesel fuel has a broader spectrum extending to n - C_{33} , with a higher proportion of lower molecular weight components (n - C_{10-22} , maximizing at C_{19}). According to these results, unburned lubricating oils from vehicle exhausts would be the major hydrocarbon source of the semi-volatile phase and important contributors to the particulate phase in our samples. To evaluate the distribution of the

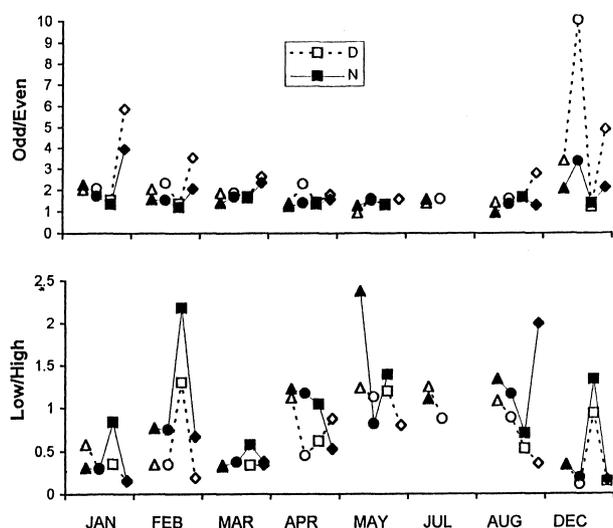


Fig. 5. Odd/Even and Low/High molecular weight ratios of airborne ALIp and ALIsv in the four stations and eight sampling months.

samples according to the different contribution of petrogenic and biogenic sources, a principal component analysis was performed using a correlation matrix of the percent hydrocarbon composition of the samples. The first two components explained 82% of the total variance, 63% the first and 19% the second. Both components clearly reflect the contribution of biogenic (+ component 1) and petrogenic sources (– component 1), including both vehicular exhaust (+ component 2) and diesel fuel (– component 2; Fig. 4). ALIsv are almost entirely derived from petrogenic sources (exhaust emissions and diesel fuel) whereas particulate hydrocarbons reflect a mixed contribution from biogenic and petrogenic sources.

The detailed view of ALIsv do not show any clear differentiation between stations but reveals an interesting day-night trend: diurnal samples are generally enriched in exhaust emissions whereas a proportionally higher contribution of crude fuel is observed during the night. Particulated hydrocarbons show a rather compact cluster of 29 samples with strong biogenic signature (bottom-right), best represented by samples collected at the residential site (9 points) and during the day (17 samples), and a transition arc of 29 samples with increasing proportion of petrogenic compounds (top-left), dominated by samples collected at the downtown and port sites (9 points each) and during the night (17 samples). The significant contribution of petrogenic hydrocarbons from mobile sources in La Plata area is favored by the obsolescence of the local automobile fleet which has little proportion of catalyst-equipped units, and the intense circulation of diesel-powered buses. Both, noncatalyst autos and diesel trucks emit 7–40 times more fine particulate *n*-alkanes (689 and 3755 $\mu\text{g}/\text{km}$, respectively) than catalyst-equipped units (109 $\mu\text{g}/\text{km}$; Rogge et al., 1993).

The evolution of the ALIp composition along the year at all four stations is traced by the Odd/Even (higher values indicate stronger biogenic inputs) and Low/High molecular weight ratios ($\langle n\text{-C}_{25} \rangle / n\text{-C}_{26}$, higher values indicate a stronger contribution from petrogenic sources; Fig. 5). The Odd/Even ratio shows a rather uniform background value of 1–1.5. The Downtown site show the lowest and more constant values (1.4 ± 0.2) whereas the other stations show higher, more variable ratios (Port = 1.7 ± 0.6 , Petrochemical = 2.5 ± 2.2 , Residential = 2.8 ± 1.4). The absence of odd predominance (Odd/Even ~ 1) is characteristic of fossil fuels and automobile exhaust particulate matter (Simoneit, 1984 and 1985; Simoneit et al., 1991); the almost constant low values registered at the Downtown site thus reflect the permanent predominance of these inputs. In the other stations, the contribution of biogenic hydrocarbons rises the averages introducing a larger variability. The Odd/Even ratios display a seasonal pattern: the values increase in summer months when plants are in complete activity and have fully-grown leaves as opposed to the fall and winter period. The Odd/Even ratio of ALIsv are very uniform during the day or night periods, in all stations and months (global average = 1.1 ± 0.2 ; Table 1) reflecting the clear prevalence of petrogenic sources.

The Low/High molecular weight ratio show a general trend of increasing values from January and February–May, July, August with a subsequent decrease in December. This trend is related to the behavior of the Odd/Even ratios indicating a higher relative contribution of lower molecular weight *n*-alkanes from petrogenic sources during fall and winter periods when plant inputs are minimal (lowest Odd/Even ratios). Over this general pattern, there are some punctual higher values, particularly at the Downtown site, which indicate a stronger contribution of petrogenic hydrocarbons. A comparable temporal trend of higher concentrations of airborne polycyclic aromatic hydrocarbons in fall and winter months has been previously reported for La Plata city (Catoggio et al., 1989).

These data on the composition of particulate and ALIsv give a consistent picture of the relative abundance of both principal hydrocarbon sources: plant material, predominating in the particulate phase during summer months and at the residential station, and fossil fuels, present in both phases, but dominant in the semi-volatile fraction, most abundant in fall and winter months and specially at the Downtown site. These compositional trends help to further interpret the variability of the data: the lower incidence of day-night differences during summer months would thus be related to a higher proportion of biogenic material in the airborne particulate matter. The larger day-night differences registered at the Downtown station reflects the enhanced input from anthropogenic sources (vehicles)

and resuspension of dust particles during the day hours of most intense human activity. The strong incidence of mobile vs. stationary sources of airborne particles and hydrocarbons in the area reflects the major commercial and administrative character of La Plata city.

References

- Aboul-Kassim, T.A.T., Simoneit, B.R.T., 1995. Aliphatic and aromatic hydrocarbons in particulate fallout of Alexandria, Egypt: sources and implications. *Environ. Sci. Technol.* 29, 2473–2483.
- Catoggio, J.A., Succar, S.D., Roca, A., 1989. Polynuclear aromatic hydrocarbon content of particulate matter suspended in the atmosphere of La Plata, Argentina. *Sci. Total Environ.* 79, 43–58.
- Colombo, J.C., Pelletier, E., Brochu, C., Khalil, M., Catoggio, J.A., 1989. Determination of hydrocarbon sources using *n*-alkane and polyaromatic hydrocarbon distribution indexes. Case study: Río de la Plata Estuary, Argentina. *Environ. Sci. Technol.* 23, 888–894.
- Dickhut, R.M., Gustafson, K.E., 1995. Atmospheric washout of polycyclic aromatic hydrocarbons in the Southern Chesapeake Bay region. *Environ. Sci. Technol.* 29, 1518–1525.
- Dockery, D.W., Pope, C.A., 1994. Acute respiratory effects of particulate air pollution. *Annu. Rev. Public Health* 15, 107–132.
- Great Lakes Center for Occupational and Environmental Safety and Health, 1997. Airborne particulate matter. *Health Effects Review*, 2(4). School of Public Health, University of Illinois at Chicago, pp. 1–7.
- Gogou, A., Stratigakis, N., Kanakidou, M., Stephanou, E.G., 1996. Organic aerosols in Eastern Mediterranean: components source reconciliation by using molecular markers and atmospheric back trajectories. *Org. Geochem.* 25, 79–96.
- Poster, D.L., Baker, J.E., 1996. Influence of submicron particles on hydrophobic organic contaminants in precipitation. 1. Concentrations and distributions of polycyclic aromatic hydrocarbons and polychlorinated biphenyls in rainwater. *Environ. Sci. Technol.* 30, 341–348.
- Poster, D.L., Baker, J.E., 1996. Influence of submicron particles on hydrophobic organic contaminants in precipitation. 2. Scavenging of polycyclic aromatic hydrocarbons by rain. *Environ. Sci. Technol.* 30, 349–354.
- Reichhardt, T., 1995. Weighing the health risks of airborne particulates. *Environ. Sci. Technol.* pp. 360A–364A.
- Rogge, W.F., Hildemann, L.M., Mazurek, M.A., Cass, G.R., 1993. Sources of fine organic aerosol. 2. Noncatalyst and catalyst-equipped automobiles and heavy-duty diesel trucks. *Environ. Sci. Technol.* 27, 636–651.
- Schauer, J.J., Rogge, W.F., Hildemann, L.M., Mazurek, M.A., Cass, G.R., Simoneit, B.R.T., 1996. Source apportionment of airborne particulate matter using organic compounds as tracers. *Atmos. Environ.* 30, 3855–3877.
- Simoneit, B.R.T., 1984. Organic matter of the troposphere – III. Characterization and sources of petroleum and pyrogenic residues in aerosols over the western US. *Atmos. Environ.* 18, 51–67.
- Simoneit, B.R.T., 1985. Application of molecular marker analysis to vehicular exhaust for source reconciliations. *Intern. J. Environ. Anal. Chem.* 22, 203–233.
- Simoneit, B.R.T., 1986. Characterization of organic constituents in aerosols in relation to their origin and transport: a review. *Intern. J. Environ. Anal. Chem.* 23, 207–237.
- Simoneit, B.R.T., 1989. Organic matter of the troposphere – V: Application of molecular marker analysis to biogenic emissions into the troposphere for source reconciliations. *J. Atmos. Chemistry* 8, 251–275.
- Simoneit, B.R.T., Mazurek, M.A., 1989. Organic tracers in ambient aerosols and rain. *Aerosol Sci. Technol.* 10, 267–291.
- Simoneit, B.R.T., Cardoso, J.N., Robinson, N., 1990. An assessment of the origin and composition of higher molecular weight organic matter in aerosols over Amazonia. *Chemosphere* 21, 1285–1301.
- Simoneit, B.R.T., Sheng, G., Chen, X., Fu, J., Zhang, J., Xu, Y., 1991. Molecular marker study of extractable organic matter in aerosols from urban areas of China. *Atm. Environ.* 25A, 2111–2129.
- Simoneit, B.R.T., Rogge, W.F., Mazurek, M.A., Standley, L.J., Hildemann, L.M., Cass, G.R., 1993. Lignin pyrolysis products, lignans, and resin acids as specific tracers of plant classes in emissions from biomass combustion. *Environ. Sci. Technol.* 27, 2533–2541.
- Takada, H., Onda, T., Ogura, N., 1990. Determination of polycyclic aromatic hydrocarbons in urban street dusts and their source materials by capillary gas chromatography. *Environ. Sci. Technol.* 24, 1179–1186.
- Webber, D.B., 1986. Dryfall: an important constituent of atmospheric hydrocarbon deposition. *Org. Geochem.* 9, 57–62.
- Westerholm, R.N., Almén, J., Li, H., Rannug, J.U., Egeback, K.E., Grägg, K. Chemical and biological characterization of particulate-, semivolatile-, and gas-phase-associated compounds in diluted heavy-duty diesel exhausts: a comparison of three different semi-volatile-phase samplers. *Environ. Sci. Technol.* 25, 332–338.