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Measurement of particulate aliphatic and polynuclear aromatic hydrocarbons in Santiago de Chile: source reconciliation and evaluation of sampling artifacts

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Abstract

Using a novel sampler, particulate organic compounds were collected in Santiago de Chile from June 9 to August 10, 1997. This sampler consists of a diffusion denuder to remove gas-phase organics prior to particle collection, a Teflon filter, and a PUF cartridge downstream of the filter. PAHs and *n*-alkanes were measured using gas chromatography/mass spectrometry analysis. Volatilization of particles collected on the Teflon filter varied from 15 to 85% for both *n*-alkanes and PAHs, with strong dependence on molecular weight. The relative distribution of *n*-alkanes and the values of molecular diagnostic ratios, such as Carbon preference index, indicated a mixed origin with strong anthropogenic input. Indeed, CPI values ranged from 0.66 to 1.96 (for the whole range of *n*-alkanes). The percent contribution of leaf “wax” *n*-alkanes (4.55–20.83%) indicated the low contribution of biogenic sources. In addition, the distribution pattern of PAHs was characteristic of anthropogenic emissions. The dominant contribution of combustion-related PAHs (CPAHs), 74–84%, indicated that vehicular emissions was the major source of PAHs. © 1999 Elsevier Science Ltd. All rights reserved.

Keywords: Diffusion denuder; Sampling artifacts; Organic aerosol; *n*-alkanes; PAH

1. Introduction

Atmospheric aerosols play an important role in climate and atmospheric chemistry and have harmful effects on human health. The interaction of atmospheric particles with solar radiation affects climate changes because particles can absorb or reflect solar radiation (Charlson et al., 1992) or can act as cloud condensation nuclei (Novakov and Penner, 1993). Furthermore, particles are deposited in different regions of the human

respiratory tract and have been related to premature death, aggravated asthma, increased hospital admissions and increased respiratory problems in children (Seaton et al., 1995).

Organic compounds contribute 10–40% of the PM_{2.5} and PM₁₀ mass in polluted urban areas, while in rural areas they represent 30–50% of the PM₁₀ mass (Chow et al., 1993, 1994). Particulate organic carbon is produced from man-made activities, including petroleum residues and vehicular emissions (Rogge et al., 1993a,b), and from natural sources such as plant epicuticular waxes and resin residues (Rogge et al., 1993c). In addition, mono- and poly-functional organic compounds, characteristic of gas-to-particle reaction mechanisms, have been detected

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in the particulate phase. Of the several hundred organic compounds that have been identified in the particulate phase, sources have only been reconciled for about 40% of them (Simoneit, 1984; Schauer et al., 1996). Special attention has been paid to PAH associated with submicrometer particles and their oxygenated and nitrated derivatives due to their known carcinogenic and mutagenic properties (Finlayson-Pitts and Pitts, 1997).

The transport, deposition, and chemical transformations of semi-volatile organic compounds is extensively controlled by their gas/particle-phase partitioning (Bidleman, 1988). The semi-empirical equations commonly used to calculate the fraction in each phase presume that the mechanism involves simple physical adsorption; however, this mechanism does not apply for the case of amorphous organic particles, which are present in ambient air (Pankow and Bidleman, 1991; Seinfeld and Pandis, 1997). The exchange of semi-volatile organic compounds between the gaseous and particulate phases can cause both positive and negative sampling artifacts (Hart and Pankow, 1994). These artifacts can lead either to underestimation or overestimation of ambient concentrations (Benneth and Stockburger, 1994). Losses of the more volatile compounds due to the high-pressure drop across the collecting filter can cause an underestimation of particle concentration, especially for longer sampling times. In contrast, adsorption of gas-phase organic compounds onto glass and quartz filters can result in an overestimation of the particulate phase concentrations. It has been shown that these positive artifacts can be 10–35% for ambient atmospheres (Benneth and Stockburger, 1994). A third type of sampling artifact is the reaction of organic compounds such as PAHs, either with gases, such as nitrogen oxides (NO_x), to form nitro-PAHs, or with ozone (O_3) and other oxidants to form oxy-PAHs (Finlayson-Pitts and Pitts, 1997). Reaction of PAHs collected on filter media with acidic gases and ozone present in air samples can result in the formation and therefore the detection of highly polar and mutagenic compounds.

Because of these artifacts, more sophisticated sampling techniques are needed for the accurate measurement of organic species (Eatough et al., 1993). To minimize sampling artifacts, diffusion denuders have been used to remove gas-phase species prior to collecting the particulate phase on a filter medium (Coutant et al., 1989). Furthermore, compounds vaporizing from the particles collected on the filter is trapped downstream on a sorbent trap. Although denuders have been widely used for inorganic gas collection (Koutrakis et al., 1993), they have two serious limitations in sampling organic compounds. First, since many of the compounds of interest are relatively non-polar, finding an appropriate denuder coating is challenging. Second, since semi-volatile organic molecules have low diffusion coefficients ($D \leq 0.05 \text{ cm}^2 \text{ s}^{-1}$), relatively low sampling rates are required. As a result,

long sampling times are necessary to achieve sufficient analytical sensitivity for species exhibiting low ambient concentrations.

The specific objectives of this study were (i) to identify the sources of particulate aliphatic and polynuclear aromatic hydrocarbons in Santiago de Chile; and (ii) to assess the volatilization losses of aliphatic and polynuclear aromatic hydrocarbons from Teflon filters during sampling, and evaluate the effect of sampling artifacts on the reliability of the study of the occurrence of particle-associated aliphatic and polynuclear aromatic hydrocarbons (PAH) in the urban environment. A diffusion denuder was used for the removal of vapor-phase semi-volatile organic compounds prior to particle collection. Molecular diagnostic ratios, including the carbon preference index (CPI) and running *odd-to-even* predominance (OEP) ratios, were used for the reconciliation of compound sources. PAHs present in the ambient aerosol samples were assigned to specific sources using molecular diagnostic ratios. Atmospheric photo-chemical reactions of non-substituted PAHs with ozone and nitrogen oxides can decrease their ambient concentrations. This effect may invalidate source apportionment studies that rely only on the measured concentrations of these non-substituted PAHs (Kamens et al., 1988; McDow et al., 1994). However, this effect can be minimized by the use of molecular diagnostic ratios. These ratios were measured in both tunnel/chamber and field studies and they are well correlated, indicating that they can be used to reconcile sources of PAHs (Rogge et al., 1993a–c; Sicre et al., 1987; Gogou et al., 1996).

2. Experimental and analytical techniques

2.1. Sampling of organic aerosols

Samples were collected from June 9 to August 10, 1997 in the residential area of Las Condes–Vitacura at the site Estadio Corfo, which belongs to the Air Quality Monitoring Network managed by the Environmental Health Service for the Metropolitan Region (SESMA). This site is located NE from downtown Santiago, in a narrow valley – Mapocho valley (802 m a.s.l.) leading to the Andes range. Since wind circulations (mountain-valley breeze conditions) are determined by orographical structures, the narrow valley in Las Condes enforces wind flow patterns coming from downtown Santiago and passing the measurement site at Estadio Corfo. Usually, this happens for some hours during the afternoon under prevailing mountain-valley breeze conditions. At this site, SESMA routinely measures O_3 , NO_x , CO , SO_2 , PM_{10} , $\text{PM}_{2.5}$, meteorological parameters and other atmospheric parameters with commercially available instruments.

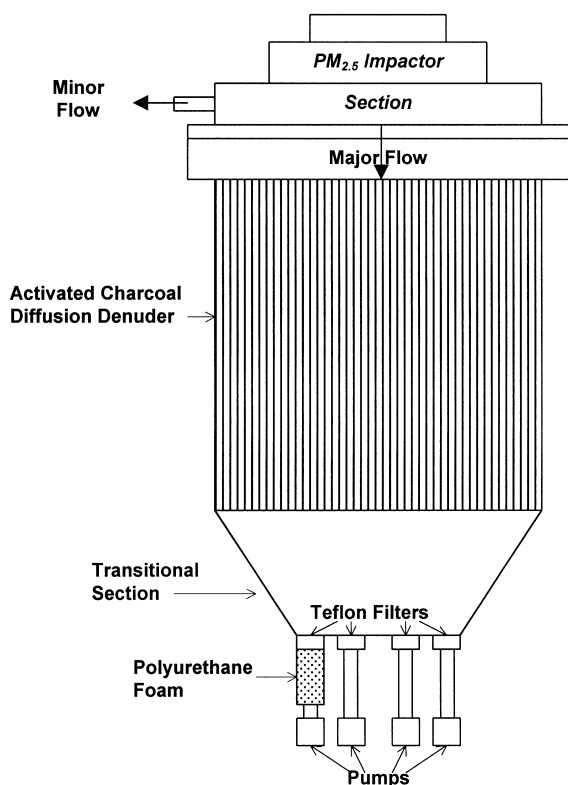


Fig. 1. Schematic diagram of the sampler equipped with the activated charcoal diffusion denuder to remove organic vapors.

Thirty 12-h and 24-h samples were collected using a high volume virtual impactor sampler (HVVI) (Fig. 1) (Marple et al., 1990). The multi-jet size-selective inlet of the HVVI was designed to provide a $2.5 \mu\text{m}$ particle size cut for a sampling flow of 1130 l min^{-1} . The sampler consists of 12 virtual impactors, each of which were operating at 93.5 l min^{-1} . For our experiment, only one of the 12 jets was used; the rest were sealed. The minor flow (5% of total flow: 4.7 l min^{-1}) contained the majority of coarse particles ($d_p > 2.5 \mu\text{m}$) and 5% of fine particles ($d_p < 2.5 \mu\text{m}$). The major flow (95% of total flow: 88.8 l min^{-1}) contained 95% of fine particles and passed through a parallel plate organic diffusion denuder. The organic denuder consisted of 60 $20.3 \times 25.4 \text{ cm}$ sheets impregnated with activated carbon (Schleicher and Schuell, "Beta-Safe"). The distance between sheets was 0.32 cm . The design of this denuder is based on a recently developed organic gas denuder (Eatough et al., 1993). After the denuder, the air stream passed through a transitional section to an adaptor plate with four sampling ports. The sampling ports were used to collect multiple samples during each sampling period. The sum of the flows of the four sampling ports was 88.8 l min^{-1} (major flow). A filter pack containing a 47 mm (pore size, $1 \mu\text{m}$) Teflon filter (TFs) (Gelman Laboratories, Zefluor[®]) was attached to each sampling port. A high-volume poly-

urethane foam (PUF) sampling tube (Supelco) to trap volatilized SVOCs was placed downstream of one of the filter packs. The collection efficiency and capacity of the organic denuder had been evaluated previously using several organic compounds of different vapor pressures, diffusion coefficients, and polarities (Koutrakis et al., 1998). The results of these experiments showed that, for the tested organic compounds (from naphthalene to pyrene), the denuder has high collection efficiency and adequate capacity at ambient (50–60%) and high (85–92%) relative humidities.

2.2. Materials and quality assurance

Calibrated flowmeters were used to measure flowrates during sampling. After collection, the filters were placed in dark glass tubes. The PUF cartridges were wrapped in aluminum foil and were placed in glass tubes. Pure solvents ("SupraSolv" grade) and standard compounds (Merck, Germany) were used for extraction, separation, and identification of aliphatic and aromatic hydrocarbons. The purity of each solvent was tested before use. Silica gel (Merck, 230–400 mesh), cotton and forceps were twice pre-extracted in a Soxhlet apparatus overnight with methylene chloride and then kept in a dedicated clean glass container. Glassware used in extraction and analysis was pre-cleaned at 550°C for 12 h. Filter and PUF cartridge blanks were analyzed using the same method as the samples. Aliphatic and aromatic hydrocarbon contamination on the TFs was negligible. Some small contamination peaks were detected in the aliphatic fraction of PUF blanks, due to the use of plasticizers during foam production.

2.3. Fractionation, derivatization, and identification

Both Teflon filters and polyurethane foam plugs were extracted and analyzed separately to obtain information about evaporation losses. A detailed description of the analytical procedure used for extraction, separation, and analysis of the main lipid fractions has been published elsewhere (Gogou et al., 1998). Briefly, filters were extracted by refluxing methylene chloride for 20 h. Polyurethane foam plugs were extracted in a Soxhlet apparatus with methylene chloride for 20 h. Each organic extract containing both aliphatic and aromatic hydrocarbons was evaporated using the Kuderna–Danish method, transferred to 1 ml vial, and dried under a gentle stream of nitrogen. The total solvent organic matter was dissolved in a small aliquot of *n*-hexane and applied on the top of a glass column containing specially treated silica gel. Nitrogen pressure was adapted to elute the different compound classes. Aliphatic and polyaromatic hydrocarbons were co-eluted with *n*-hexane and a solution of toluene/*n*-hexane, respectively. All samples were analyzed on a Finnigan GCQ ion trap gas chromatography-mass

spectrometer (at the University of Crete) in electron and methane-chemical impact mode equipped with a HP-5MS capillary column (30 m × 0.25 mm i.d. × 0.25 μm film thickness). The temperature ramp was splitless injection at 270°C, oven temperature held at 70°C for 2 min, temperature increased to 150°C at a rate of 10°C min⁻¹, temperature increased to 290°C at a rate of 5°C min⁻¹ and column held at 290°C for 30 min. Flame ionization detector temperature was 290°C, mass spectrometer ion source temperature was 200°C, and electron impact ionization was 70 eV. The identification of *n*-alkanes (C₁₅–C₄₀) and PAHs was performed using reference standards (Dr.Ehrenstorfer GmbH, Germany).

2.4. Molecular diagnostic ratios

The values of molecular diagnostic ratios can be used to reconcile sources of organic species, since the distribution of homologues is strongly associated with formation mechanisms of carbonaceous aerosol. In particular,

(a) The carbon preference index (CPI) for *n*-alkanes (ratio *odd-to-even*) was calculated as follows (Bray and Evans, 1961):

- (i) whole range for *n*-alkanes: $CPI_1 = \frac{\sum(C_{13} - C_{35})}{\sum(C_{12} - C_{34})}$,
- (ii) petrogenic *n*-alkanes: $CPI_2 = \frac{\sum(C_{13} - C_{25})}{\sum(C_{12} - C_{24})}$,
- (iii) biogenic *n*-alkanes: $CPI_3 = \frac{\sum(C_{25} - C_{35})}{\sum(C_{24} - C_{34})}$.

n-Alkanes originate from epicuticular waxes of terrestrial plants and exhibit high values of CPI (CPI ≫ 1). On the other hand, CPI values for vehicular emissions and other anthropogenic activities are close to unit (CPI ≈ 1).

(b) the biogenic “wax” concentration of *n*-alkanes was calculated as follows (Simoneit et al., 1990):

$$\text{wax } C_n = C_n - 0.5 [C_{n-1} + C_{n+1}]$$

Based on this equation, the “wax” concentration of each *n*-alkane was calculated and therefore the contribution of biogenic sources was estimated.

(c) Running *odd-to-even* predominance (OEP) ratios were computed using the following equation (Scalan and Smith, 1970):

$$\text{OEP for } C_n = \frac{[(C_{n-2} + 6 \cdot C_n + C_{n+2}) / (4 \cdot C_{n-1} + 4 \cdot C_{n+1})]^{(-1)^{(n-1)}}$$

OEP values were plotted vs. carbon chain length to construct the OEP curves. The pattern of OEP curve is determined by the source of *n*-alkanes (Scalan and Smith, 1970; Kavouras et al., 1998)

(d) The ratio of total concentration of nine combustion PAH (CPAH) (fluoranthene, pyrene, benzo[a]anthracene, chrysene, benzo[fluoranthene], benzo[a]pyrene, benzo[e]pyrene, indeno[cd]pyrene and benzo[ghi]perylene) to the total concentration of PAH (TPAH)

(CPAH/TPAH) was determined. The value of CPAH/TPAH ratio calculated for non-catalyst (0.41) and catalyst-equipped (0.51) automobiles and for heavy-duty diesel trucks (0.30) has been determined by Rogge et al. (1993a).

3. Results and discussion

3.1. Volatilization losses

The concentrations and percentage volatilization losses of *n*-alkanes and PAHs collected by the Teflon filter are given in Table 1. Often reported as “blow-off”, volatilization of organic compounds can result from the pressure gradient that exists through a filter, or from temperature fluctuation occurring during sampling. Compounds lost from the Teflon filter are collected on the sorbent (PUF) downstream of the filter. Because the diffusion denuder is used upstream of the filter to remove organic vapors, the gas/particle equilibrium is shifted, potentially causing greater volatilization losses than would occur without the denuder.

3.1.1. Aliphatic hydrocarbons

n-Alkanes ranged from C₁₆ to C₃₅ were detected in both Teflon filter (TFs) and the PUF cartridge samples. Concentrations of C₁₉–C₃₀ *n*-alkanes in PUF cartridges were higher than for the TFs (Table 1). The opposite was true for higher molecular weight particulate *n*-alkanes (> C₃₁), as shown by the same table (Table 1). These results suggest, as expected, that losses depend upon the volatility of the species. Assuming that the total ambient particulate concentration is equal to the sum of TFs and PUFs concentrations for C₂₁–C₃₅ *n*-alkanes, volatilization losses represent 20–80% of the total concentrations (Table 1).

The characteristic relative distribution of *n*-alkanes as the sum of TFs and PUFs (corrected) and only TFs (uncorrected) for two different samples are given in Fig. 2a and b, respectively. When volatilization losses are not considered, the relatively small amounts of *n*-alkanes for < C₂₇ (uncorrected; Fig. 2a and b) would indicate that the contribution of vehicular emissions is negligible, and unburned fossil fuel and direct emissions of terrestrial plant epicuticular waxes are the major sources; however, the corrected pattern of *n*-alkanes (corrected; Fig. 2a and b) indicates that contribution of fossil fuel combustion is quite significant.

The mixture of unresolved branched, cyclic and unsaturated hydrocarbons (UCM: unresolved complex mixture) is also an important parameter to reconcile the sources of aliphatic hydrocarbons. Since unresolved hydrocarbons are emitted from combustion processes and can be both volatile and semi-volatile organic compounds, it is possible that losses of UCM can occur during sampling. Indeed, concentrations of UCM

Table 1
Concentration and percentage volatilization losses of *n*-alkanes and PAHs collected by the Teflon filter (TFs) and polyurethane foam (PUFs)

<i>n</i> -Alkanes				Polynuclear Aromatic Hydrocarbons			
Compound (MW)	TFs conc. (ng m ⁻³)	PUFs Conc. (ng m ⁻³)	% Volatilization losses	Compound (MW)	TFs conc. (ng m ⁻³)	PUFs conc. (ng m ⁻³)	% Volatilization losses
C ₂₁ (296)	0.72–7.07	10.13–16.36	81.75 ± 15.01	Phenanthrene (172)	0.01–0.08	0.18–1.54	89.40 ± 10.64
C ₂₂ (310)	0.96–22.19	28.53–68.73	83.24 ± 23.41	Anthracene (172)	0.00–0.01	0.00–0.04	97.29 ± 3.83
C ₂₃ (324)	1.08–22.99	40.50–75.68	86.56 ± 19.72	Methyl-phenanthrene (192)	0.03–0.14	1.95–6.45	97.39 ± 3.46
C ₂₄ (338)	0.95–34.24	45.36–111.25	84.82 ± 24.10	Dimethyl-phenanthrene (206)	0.38–0.57	0.44–2.97	74.02 ± 20.41
C ₂₅ (352)	0.48–37.65	54.25–132.18	85.88 ± 23.26	Fluoranthene (202)	0.02–0.05	0.02–0.22	57.74 ± 33.74
C ₂₆ (366)	0.21–34.56	58.63–134.00	86.76 ± 20.69	Pyrene (202)	0.02–0.05	0.02–0.09	56.33 ± 30.68
C ₂₇ (380)	2.92–38.64	58.09–139.74	83.00 ± 20.17				
C ₂₈ (394)	5.25–30.73	43.59–105.45	77.02 ± 18.30				
C ₂₉ (408)	12.07–44.76	29.09–79.99	65.87 ± 18.39				
C ₃₀ (422)	22.05–59.17	13.45–55.87	49.63 ± 19.29				
C ₃₁ (436)	13.25–75.90	2.51–41.97	39.97 ± 31.84				
C ₃₂ (450)	8.75–64.27	0.01–25.10	27.24 ± 30.24				
C ₃₃ (464)	4.23–65.56	0.01–15.19	29.84 ± 40.67				
C ₃₄ (478)	4.11–33.99	0.01–33.99	25.05 ± 29.76				
C ₃₅ (492)	3.51–22.17	0.01–4.56	20.52 ± 11.84				

collected on TFs are lower ($871.71 \pm 409.28 \text{ ng m}^{-3}$) than those calculated for PUFs ($2476.66 \pm 1344.16 \text{ ng m}^{-3}$). These results indicate that evaporation losses of UCM are important (73.96%) and are comparable to those measured for C₁₉–C₂₆ *n*-alkanes (Table 1). UCM/*n*-alkanes (UCM/NA) ratios calculated for aliphatic hydrocarbons collected onto TFs (4.45 ± 3.44) are similar to those calculated for PUFs (3.46 ± 0.37), and indicate the importance of vehicular emissions. The fluctuation of TFs UCM/NA ratios (S.D. = 3.44) values is strongly controlled by the relative contribution of sources. On the other hand, the values of PUFs UCM/NA ratios do not fluctuate (S.D. = 0.37) because they depend upon only the physical desorption properties of the *n*-alkanes and UCM collected by the TFs. These results indicate that measured concentrations of UCM are seriously underestimated if only TFs are used for collection.

3.1.2. Polycyclic aromatic hydrocarbons

PAHs collected on TFs contained mostly 4- and 5-ring compounds while 2- and 3-ring PAHs were collected mostly on PUF cartridges. The main reason for finding no detectable concentrations of higher molecular weight PAHs for the PUF cartridges is because these compounds exhibit low volatility (Fig. 2c and d). Volatilization losses of relatively volatile PAHs, such as phenanthrene and anthracene, varied from 78 to 98% (Fig. 2c,d and Table 1).

The ratio of methyl-phenanthrene to phenanthrene (MPh/Ph) is an indicator of PAH origin. The ratio of MPh/Ph for TFs was 2.28 ± 1.15 , which corresponds to emissions from catalyst-equipped automobiles (Rogge et al., 1993a), while the MPh/Ph ratio for PUFs was

7.37 ± 3.77 , which is characteristic of emissions from unburned petroleum residues (Rogge et al., 1993a; Grimmer et al., 1983). These results suggest the importance of using an organic gas denuder device and a sorbent behind the filter media to accurately determine the concentrations of particulate organics and their sources based on molecular diagnostic ratios.

3.2. Source reconciliation

Table 2 reports the following results for samples collected in Santiago de Chile (a) corrected concentration ranges; and (b) molecular diagnostic ratios for both *n*-alkanes and PAH.

3.2.1. Aliphatic hydrocarbons

All samples were dominated by *n*-alkanes (C₁₆–C₃₆) with a significant contribution of an unresolved complex mixture (UCM), which appears as a broad envelope, consisting of cyclic, unsaturated and branched alkanes. Maximum *n*-alkane concentration varied from C₂₅ to C₃₁ (Table 2). This variability is due to differing relative contribution of the anthropogenic and biogenic sources. Concentrations of particle-associated *n*-alkanes varied from 452.30 to 1439.12 ng m⁻³. Lower concentrations of *n*-alkanes were measured during rainfall events. In general, concentrations determined in Santiago de Chile were higher than those measured in other urban areas such as Pasadena (Rogge et al., 1993a–c) and Heraclion (Gogou et al., 1996; Kavouras et al., 1998), and higher than those measured in suburban and rural areas in Crete (Gogou et al., 1996; Kavouras et al., 1998). These high concentrations of *n*-alkanes measured in Santiago

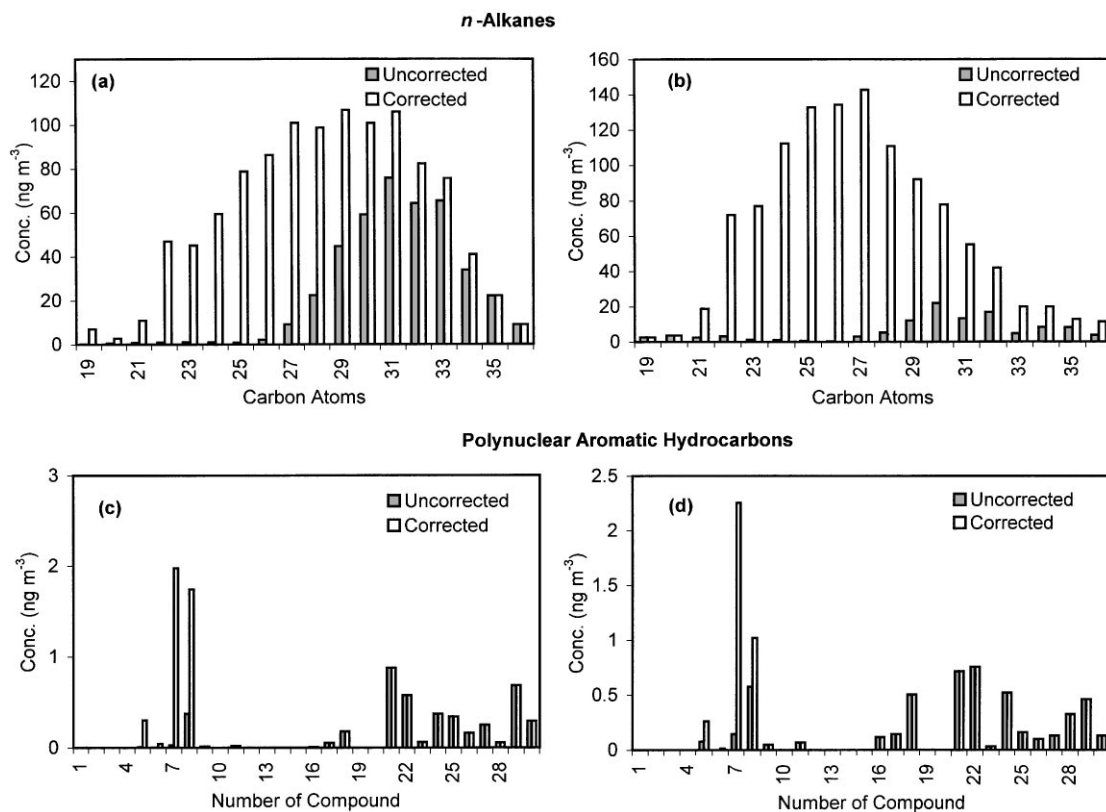


Fig. 2. Concentration distribution pattern of *n*-alkanes (a, b) and PAHs (c, d) collected on TFs (uncorrected) and the sum of the concentrations of TFs and corresponding PUFs (corrected).

de Chile indicated that contribution of anthropogenic emissions is high, and this is in agreement with the measurements of gaseous aromatic hydrocarbons in Santiago emitted by vehiculars (Rappengluck et al., 1999).

None of the samples showed an *odd-to-even* predominance for the whole range of *n*-alkanes (Fig. 3a). The CPI_1 values (ranged from 0.66 to 1.96; Table 2) were similar to those observed for other urban areas (Kavouras et al., 1998). This underscores the importance of petroleum and diesel residues and gasoline emissions and the minor contribution of *n*-alkanes emitted directly from epicuticular waxes. In addition, the CPI_2 values for petrogenic hydrocarbons, varied between 0.51 and 1.44 as shown in Table 2, indicate that emissions from anthropogenic activities are more important than terrestrial plants. This is further supported by the presence of the unresolved complex mixture (UCM). Indeed, the values of the UCM/NA ratio in our samples varied from 0.00 to 9.93 (Table 2) and they are within the range measured for unburned fossil fuels emitted by vehicles.

CPI_3 values for biogenic *n*-alkanes varied between 0.65 and 4.00, suggesting that mechanical abrasion of organic lipids from leaf epicuticular waxes is the predominant source for this *n*-alkane range. To determine the relative

importance of biogenic and petrogenic sources, the contribution of wax terrestrial *n*-alkanes (WAX) were estimated. The contribution of biogenic wax *n*-alkanes to the total *n*-alkanes concentration in Santiago de Chile ranged from 4.55 to 20.83%, indicating that emissions from epicuticular waxes of terrestrial plants had a lower input to the ambient organic aerosol concentration (for comparison see Gogou et al., 1996). The observed odd-to-even predominance (OEP) curve shown in Fig. 3b is quite similar to those found for other urban areas (Kavouras et al., 1998), suggesting the importance of anthropogenic sources.

3.2.2. Polynuclear aromatic hydrocarbons

A characteristic chromatogram of polynuclear aromatic hydrocarbons collected on a Teflon filter is presented in Fig. 4a. The collected PAHs identified in the analyzed samples had total concentrations from 0.68 to 11.14 ng m⁻³. Although, a large number of parent and methylated PAHs (from phenanthrene to coronene) were detected in our study, PAHs concentrations measured in Santiago de Chile are lower than those measured in other cities, such as in Pasadena (Rogge et al., 1993a–c), Los Angeles (Grosjean, 1983), Munich (Steinmetzer et al.,

Table 2
Concentration ranges and molecular diagnostic ratios of *n*-alkanes and PAHs

<i>n</i> -Alkanes		Polynuclear Aromatic Hydrocarbons	
	Conc. (ng m ⁻³)		Conc. (ng m ⁻³)
C ₁₆	1.05–5.01	Naphthalene	0.00–0.00
C ₁₇	1.10–8.11	Methyl-naphthalene	0.00–0.00
C ₁₈	1.50–9.73	Acenaphthene	0.00–0.00
C ₁₉	1.85–13.35	Fluorene	0.00–0.00
C ₂₀	2.25–19.63	Phenanthrene	0.00–1.54
C ₂₁	9.86–23.48	Anthracene	0.00–0.04
C ₂₂	10.12–90.36	Methyl-phenanthrene	0.01–6.38
C ₂₃	44.58–97.86	Dimethyl-phenanthrene	0.13–3.25
C ₂₄	47.24–136.90	Fluoranthene	0.00–0.23
C ₂₅	56.43–159.10	Acphenanthrylene	0.00–0.00
C ₂₆	60.83–168.56	Pyrene	0.00–0.07
C ₂₇	63.96–178.00	Trimethyl-phen/Anthracene	0.00–0.00
C ₂₈	53.68–132.41	Methyl-pyrene	0.00–0.00
C ₂₉	43.23–118.23	Dimethyl-fluor/Pyrene	0.00–0.00
C ₃₀	38.95–110.87	Benzo[ghi]fluorene	0.00–0.00
C ₃₁	18.75–115.98	4-(H)-cyclopenta[cd]pyrene	0.00–0.12
C ₃₂	8.76–87.63	Benzo[a]anthracene	0.01–0.14
C ₃₃	4.24–80.23	Chrysene/triphenylene	0.03–0.50
C ₃₄	4.12–35.29	Octahydro-benzo[a]Pyrene	0.00–0.00
C ₃₅	3.52–29.63	Methyl-chrysene/triphenylene	0.00–0.00
C ₃₆	1.08–15.12	Benzo[b/j]fluoranthene	0.06–1.73
		Benzo[k]fluoranthene	0.07–1.34
		Benzo[a]fluoranthene	0.01–0.12
		Benzo[e]pyrene	0.03–0.86
		Benzo[a]pyrene	0.03–0.68
		Perylene	0.03–0.39
		Indeno[7,1,2,3-cdef]chrysene	0.03–0.48
		Indeno[1,2,3-cd]pyrene	0.01–0.32
		Benzo[ghi]perylene	0.10–1.32
		Coronene	0.05–0.66
Molecular diagnostic ratios			
CPI ₁	0.66–1.96	CPAHs/TPAHs	0.78 ± 0.16
CPI ₂	0.51–1.44	Ph/(Ph + An)	0.75 ± 0.18
CPI ₃	0.65–4.00	MPh/Ph	6.40 ± 2.29
UCM/NA	0.00–9.93	BaA/BaA + CT	0.16 ± 0.08
% WAX	4.55–20.83	BeP/BeP + BaP	0.45 ± 0.27
		Fl/Fl + Py	0.41 ± 0.10
		IP/IP + BgP	0.32 ± 0.22

(CPI, Carbon Preference Index, UCM, Unresolved Complex Mixture, NA, *n*-alkanes, WAX, leaf wax *n*-alkanes, CPAHs, combustion-derived PAHs, TPAHs, total PAHs, MPh/Ph, methyl-phenanthrene to phenanthrene, BA/BA + CT, benzo[a]anthracene to (benzo[a]anthracene + chrysene/triphenylene), BeP/BeP + BaP, benzo[e]pyrene to (benzo[e]pyrene + benzo[a]pyrene), Fl/Fl + Py, fluoranthene/(fluoranthene + pyrene), and IP/IP + BgP, indeno[1.2.3-cd]pyrene to (indeno[1.2.3-cd]pyrene + benzo[ghi]perylene))

1984), Copenhagen (Nielsen, 1996), Kokkola, Finland (Pyssalo et al., 1987), Birmingham, UK (Smith and Harrison, 1996), cities from the Upper Silesia region of Poland (Bodzek et al., 1993) and Heraclion (Kavouras et al., 1998). The comparison of total PAHs concentrations among other urban and rural areas is of interest because of the qualitative differences observed for PAH composition these samples contained mostly 4- and 5-ring compounds and their methylated derivatives. The PAH

distribution pattern is shown in Fig. 4b. Chrysene, benzofluoranthenes and benzopyrenes were abundant in analyzed samples. These compounds are known to be associated with combustion sources.

The sum of the concentrations of the nine major combustion PAHs (CPAH) in our samples (fluoranthene, pyrene, chrysene, fluoranthenes, benzo[a]anthracene, benzo[e]pyrene, benzo[a]pyrene and benzo[ghi]perylene) accounted for about 78% of the total PAH mass.

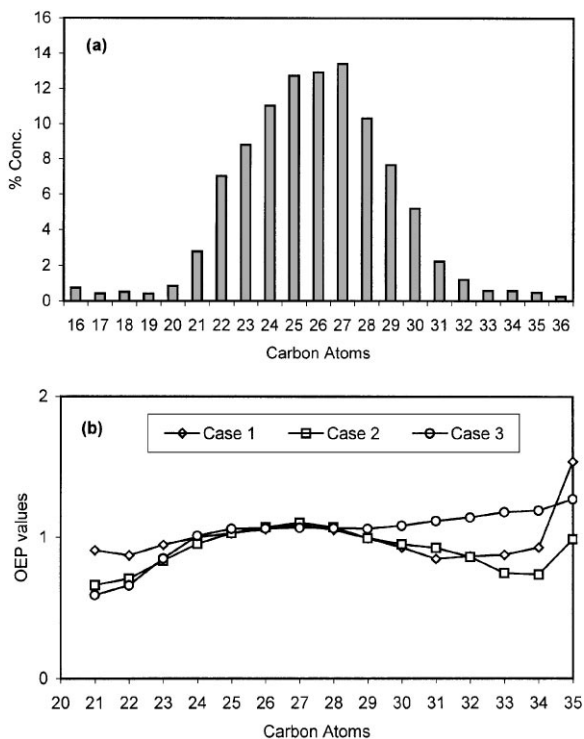


Fig. 3. Characteristic corrected distribution pattern (a) and OEP running ratio diagram (b) of *n*-alkanes in urban aerosol.

The mean CPAH/TPAH ratio was 0.78 ± 0.16 as shown in Table 2. This value is similar to that found for non-catalyst and catalyst equipped automobiles and heavy-duty diesel trucks, and indicates that combustion, rather than unburned fossil fuels, is the principle source of the observed PAH (Rogge et al., 1993a). The mean methylphenanthrene to phenanthrene ratio (MPh/Ph) in Santiago de Chile during the sampling period was 6.40 ± 2.29 (Table 2). This ratio is similar to that reported for vehicular emissions (Rogge et al., 1993a), indicating the importance of unburned fossil fuels emitted from vehicles. In addition, the pattern of dimethyl-phenanthrenes (Fig. 4c) also indicates a clear contribution from vehicular emissions with maxima at 2,6- (No. 4), 1,3- (No. 5), 2,10- (No. 6), 3,9- (No. 7) and 3,10- (No. 8) dimethyl isomers (Benner et al., 1995).

A review of other diagnostic ratios, including (a) (benzo[a]anthracene)/(benzo[a]anthracene + chrysene/(triphenylene)), [BaA/BaA + CT]; (b) (benzo[e]pyrene)/(benzo[e]pyrene + benzo[a]pyrene), [BeP/BeP + BaP]; (c) (fluoranthene)/(fluoranthene + pyrene), [Fl/Fl + Py]; and (d) (indeno[1.2.3-cd]pyrene)/(indeno[1.2.3-cd]pyrene + benzo[ghi]perylene), [IP/IP + BgP], suggests a mixed origin of unburned fossil fuel and vehicular emissions (Sicre et al., 1987; Gogou et al., 1996). In particular, the mean [BeP/BeP + BaP] ratio measured

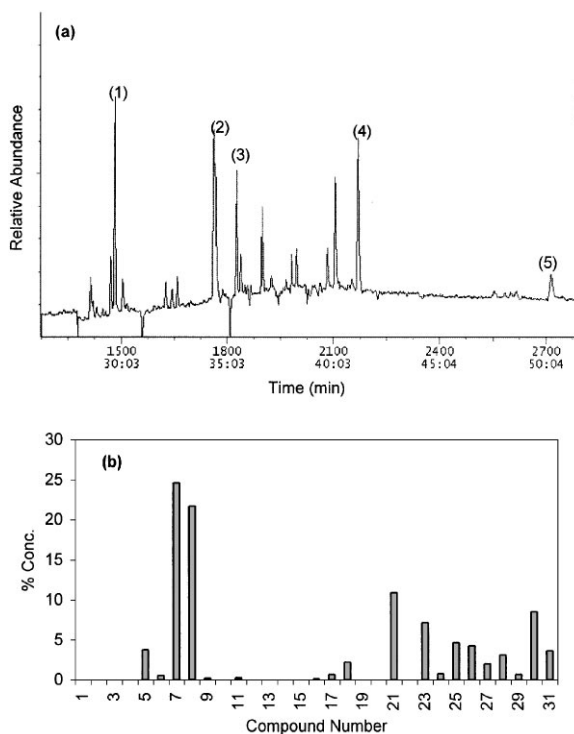


Fig. 4. Typical gas chromatogram of PAHs collected onto TFs (a), (1): chrysene/triphenylene; 2: benzofluoranthenes; 3: benzopyrenes; 4: benzo[ghi]perylene; 5: coronene), the corrected relative distribution of PAHs (b) (1: naphthalene; 2: methyl-naphthalene; 3: acenaphthene; 4: fluorene; 5: phenanthrene; 6: anthracene; 7: methylphenanthrene; 8: dimethylphenanthrene; 9: fluoranthene; 10: acephenanthrylene; 11: pyrene; 12: trimethyl phen-anthracene; 13: methylpyrene; 14: dimethyl fluor-pyrene; 15: benzo[ghi]fluorene; 16: 4-H-cyclopenta[cd]pyrene; 17: benzo[a]anthracene; 18: chrysene/triphenylene; 19: octahydrobenzo[a]pyrene; 20: methylchrysene/triphenylene; 21: benzo[b/j] fluoranthene; 22: benzo[k]fluoranthene; 23: benzo[a] fluoranthene; 24: benzo[e]pyrene; 25: benzo[a]pyrene; 26: perylene; 27: indeno[7,1,2,3-cde]chrysene; 28: indeno[1.2,3-cd]pyrene; 29: benzo[ghi]perylene; 30: coronene) and the distribution of dimethyl-phenanthrenes (MW 206) (c) in urban aerosol.

in this study was 0.45 ± 0.27 (Table 2). This suggests the importance of petroleum combustion residues. The mean [Fl/Fl + Py] ratio was 0.41 ± 0.10 (Table 2), which is similar to that reported for vehicular emissions and especially for catalytic automobiles (Rogge et al., 1993b). The literature reported values for [IP/IP + BgP] are 0.18, 0.37 and 0.56, for cars, diesel, and coal, respectively (Grimmer et al., 1983). The mean ratio obtained in our study was 0.32 ± 0.22 (Table 2), which is comparable to that for diesel emissions. Photochemical reactions of PAHs can be an important limitation to source reconciliation studies. However, the results reported here confirm previously reported results (Rogge et al., 1993a–c; Sicre et al., 1987; Gogou et al., 1996) that when a series of molecular diagnostic ratios for PAHs are used to distinguish between different sources, the results are the same as for less reactive PAHs. Overall, our results suggest that the major source of organic aerosol in Santiago during the study period was fossil fuel combustion from automobiles, with a substantial contribution from unburned petroleum residues.

4. Conclusions

The use of a diffusion denuder prior to collecting particles on Teflon filters followed by polyurethane foam cartridges can make it possible to obtain accurate measurements of particulate phase concentrations of semi-volatile organic compounds, and to adequately reconcile their sources. These results show that volatilization losses for low molecular weight *n*-alkanes (C_{19} – C_{26}) originating from vehicular emissions are higher than losses for heavier *n*-alkanes (C_{27} – C_{35}). When using only a Teflon filter, concentrations of the more volatile particulate phase *n*-alkanes and PAHs can be seriously underestimated (50% or more). Furthermore, the relative distribution of non-volatilized *n*-alkanes (TF only) for Santiago indicated that contributions of biogenic and anthropogenic sources were comparable, while the opposite conclusion was drawn when the total (TF plus PUF) concentration was used. Thus, using only a Teflon filter may result in a significant underestimation of the contribution of anthropogenic emissions. This is due to the fact that volatile particle-associated compounds are released during fossil fuel combustion in higher proportions than those from biogenic sources.

The CPI_1 ratio indicates a predominant input of petroleum and diesel residues and gasoline emissions and a minor contribution of directly emitted *n*-alkanes from epicuticular waxes. This is in agreement with CPI_2 ratio (for petrogenic hydrocarbons) and the presence of UCM. The contribution of biogenic emissions was determined by the CPI_3 values (for biogenic *n*-alkanes) but their contribution was minor. The mean values of the CPAH/TPAH and MPh/Ph ratios are indicative of emissions from non-catalyst and catalyst equipped automobiles

and heavy-duty diesel trucks. These conclusions are further supported by the molecular diagnostic ratios of other PAHs such as [BaA/BaA + CT], [BeP/BeP + BaP], [Fl/Fl + Py] and [IP/IP + BgP]. In conclusion, vehicular emissions was the major source of fine organic aerosol ($d_p < 2.5 \mu m$) in Santiago de Chile during the study period, while the contribution of epicuticular waxes emitted by terrestrial plants was minor.

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