



PERGAMON



Atmospheric Environment 36 (2002) 3851–3863

**ATMOSPHERIC
ENVIRONMENT**

www.elsevier.com/locate/atmosenv

The composition and sources of PM_{2.5} organic aerosol in two urban areas of Chile

Manolis Tsapakis^a, Evaggelia Lagoudaki^a, Euripides G. Stephanou^{a,*},
Ilias G. Kavouras^b, Petros Koutrakis^b, Pedro Oyola^c, Dietrich von Baer^d

^aEnvironmental Chemical Processes Laboratory (ECPL), Department of Chemistry, University of Crete, 71409 Heraclion, Greece

^bEnvironmental Science and Engineering Program, Harvard School of Public Health, 665 Huntington Avenue, Boston, MA 02115, USA

^cComisión Nacional del Medio Ambiente, Región Metropolitana, Valentin Letelier 13, Santiago de Chile, Chile

^dFacultad de Farmacia, Universidad de Concepcion, Casilla 160-C, Concepcion, Chile

Received 22 November 2001; accepted 29 March 2002

Abstract

Fine particle (PM_{2.5}) samples were collected, using a charcoal diffusion denuder, in two urban areas of Chile, Santiago and Temuco, during the winter and spring season of 1998. Molecular markers of the organic aerosol were determined using GC/MS. Diagnostic ratios and molecular tracers were used to investigate the origin of carbonaceous aerosols. As main sources, road and non-road engine emissions in Santiago, and wood burning in Temuco were identified. Cluster analysis was used to compare the chemical characteristics of carbonaceous aerosols between the two urban environments. Distinct differences between Santiago and Temuco samples were observed. High concentrations of isoprenoid (30–69 ng m⁻³) and unresolved complex mixture (UCM) of hydrocarbons (839–1369 ng m⁻³) were found in Santiago. High concentrations of polynuclear aromatic hydrocarbons (751 ± 304 ng m⁻³) and their oxygenated derivatives (4 ± 2 ng m⁻³), and of *n*-alk-1-enes (16 ± 13 ng m⁻³) were observed in Temuco. © 2002 Elsevier Science Ltd. All rights reserved.

Keywords: PM_{2.5}; Organic aerosol; Polynuclear aromatic hydrocarbons; Oxygenated polynuclear aromatic compounds; *n*-alk-1-enes; Charcoal denuder; Cluster analysis

1. Introduction

Large amounts of particulate matter (PM) are emitted into the atmosphere of populated and industrialized urban areas. Air quality standards for PM were expressed in terms of total suspended particulate matter (TSP). In the United States, the standard was changed to mass of suspended particulate matter < 10 μm in size (PM₁₀) and recently PM < 2.5 μm in diameter (PM_{2.5}) was included (US-EPA, 2000). The rationale for basing these air quality standards is based on the health effects,

which could be associated with PM₁₀ and PM_{2.5} (US-EPA, 2000). Organic compounds of biogenic and anthropogenic origin often represent a large fraction, up to 40%, of total PM mass (Chow et al., 1993, 1994) with concentrations ranging from a few pg m⁻³ to hundreds ng m⁻³ (Nielsen, 1996; Gogou et al., 1996, 1998; Kavouras et al., 1998a, 1999a; Zheng et al., 2000). Anthropogenic emissions include fossil fuel (diesel and gasoline) combustion from mobile and stationary sources (Simoneit, 1985; Rogge et al., 1993a–c), biomass burning (forest fires, landfills, agricultural activities and incinerators) (Oros and Simoneit, 1999) and natural gas (Rogge et al., 1993c), wood (McDonald et al., 2000; Purvis and McCrillis, 2000) and coal (Mastral and Callen, 2000) combustion. Wind erosion of leaf epicuticular waxes, vegetation debris, microbial degradation

*Corresponding author. Tel.: +30-81-393628; fax: +30-81-393678.

E-mail address: stephanou@chemistry.uoc.gr (E.G. Stephanou).

and volcanoes eruption are considered as the most important biogenic sources (Simoneit and Mazurek, 1982; Simoneit et al., 1990; Rogge et al., 1993d). Particulate phase organics can also be produced through photo-oxidation reactions of unsaturated natural organic compounds (e.g. terpenes, unsaturated organic acids, etc.), which are precursors of carbonaceous aerosol (Kawamura and Gagosian, 1987; Stephanou and Stratigakis, 1993; Stephanou, 1992; Kavouras et al., 1998a, b, 1999b, c).

Chile is one of the most urbanized and industrialized countries in South America, with almost 90% of the population residing in large urban areas. The growing Chilean economy is due to the rapid growth of industrial activities, which have adversely impacted the air quality in many urban areas (Artaxo et al., 1999; Kavouras et al., 1999c, 2001a, b). Recent source apportionment studies conducted in Santiago and Temuco suggest that sulfur-/chlorine-related sources and traffic emissions accounted for more than 70% of PM_{2.5} mass concentration (Artaxo et al., 1999; Kavouras et al., 2001a). Furthermore, combustion sources, fugitive emissions and unburned fossil fuel were the most important sources of PAHs and aliphatic hydrocarbons (Kavouras et al., 1999a, 2001b) in Santiago. Also, these studies found that automobile and wood burning emissions accounted for up to 50% of PM_{2.5} in Temuco.

In the present study we have characterized and compared the composition of organic fraction of PM_{2.5} atmospheric particles in Santiago and Temuco. Concentrations were determined using gas chromatography/mass spectrometry (GC/MS) (Gogou et al., 1998). Anthropogenic and biogenic sources were identified using molecular markers and specific compounds concentration diagnostic ratios (Sicre et al., 1987; Rogge et al., 1993a–d; Gogou et al., 1996). Cluster analysis was used to investigate the differences in the chemical composition of organic aerosols of the two cities.

2. Sampling and analytical methods

Nineteen (19) 24-h particle samples were collected during the periods of: (a) 6–20 August 1998; (b) 31 August–5 September 1998; and (c) 22–28 October 1998 in both Santiago and Temuco. Santiago is the capital of Chile with a population of approximately 5,000,000 inhabitants (about 50% of total population of Chile) and about 1,000,000 motor vehicles. It is located in central Chile (33.5°S 70.6°W), in a narrow valley at the bottom of Andes (up to 3000 m height), about 150 km east of the Pacific Ocean. Major industrial facilities, including copper smelters and oil refineries, power plants and chemical industries, are located throughout the metropolitan area of Santiago. Temuco is an urban area of 210,000 inhabitants, and is located at the

southern part of Chile, approximately 800 km south of Santiago. There are no industrial facilities in the area, which is in a valley surrounded by forested mountains.

In Santiago, particle samples were collected at the Huerfanos (on the top of a 10-level building), which is located in the central area of McIver (commercial and public services). In Temuco, at the site Navarra/San Martín, in a residential area at the northwest border of Temuco, samples were taken at a height of 1.5 m from surface level. Particle-associated organic compounds were collected using a recently developed sampler. In this device, gaseous organic compounds are removed prior to particle collection using a plate-and-frame activated charcoal diffusion denuder (Eatough et al., 1993; Kavouras et al., 1999a). Particles were collected on a 47-mm (1 µm pore size) Teflon filter (TFs) (German Laboratories, Zefluor[®]) followed by a polyurethane foam cartridge (PUF: 76 mm [H] × 65 mm [OD]; density: 0.022 g cm⁻³) in a sampling tube (Supelco[®], Inc.). The particle-sampling device has been previously described (Koutrakis et al., 1998, 1999a). After sampling, both collection media (TFs and PUF) were wrapped with aluminum foil and stored at -30°C in airtight glass jars. Separation and identification of the specific organic compounds was performed according to the analytical protocol described in detail by Gogou et al. (1998). All samples were analyzed by using a HP 5890 gas chromatograph (GC) interfaced to a HP 5971A mass-selective detector (MSD) in the electron ionization (EI) mode (ionization energy, 70 eV) and a Finnigan GCQ ion trap gas chromatograph-mass spectrometer in the MS/MS mode (oxygenated polyaromatic hydrocarbons). Individual organic compounds were identified by comparing their mass spectra to those obtained from reference standards.

3. Molecular diagnostic parameters and data analysis

In order to investigate the origin of organic aerosols, the following molecular markers and diagnostic parameters were used:

- (a) The wax *n*-alkanes concentration (WNA) was calculated for each *n*-alkane as follows (Simoneit, 1989; Gogou et al., 1996):

$$\text{WNA } C_n = C_n - 0.5(C_{n-1} + C_{n+1}),$$

where C_n negative values were set to zero. The percentage of total wax *n*-alkanes to total *n*-alkanes (%WNA) was also calculated as follows:

$$\% \text{WNA} = \left(\frac{\sum \text{WNA } C_n}{\sum \text{NA}} \right) 100,$$

where $\sum \text{WNA } C_n$ is the total concentration of wax *n*-alkanes and $\sum \text{NA}$ is the total concentration of *n*-alkanes.

- (b) The carbon preference index for *n*-alkanes and *n*-alkanoic acids was calculated according to Bray and Evans (1961) and Simoneit (1989) using the following equation:

(i) for *n*-alkanes

$$\text{CPI} = \frac{\sum (C_{13} - C_{35})}{\sum (C_{12} - C_{34})},$$

(ii) for *n*-alkanoic acids

$$\text{CPI} = \frac{\sum (C_{12} - C_{34})}{\sum (C_{13} - C_{35})}.$$

Carbon preference index (CPI; ratio odd-to-even) is an important parameter to specify the origin of *n*-alkanes (Gogou et al., 1996). Naturally emitted hydrocarbons exhibit values of $\text{CPI} > 1$. Conversely, CPI values for vehicular emissions and other anthropogenic activities are close or lower ($\text{CPI} \leq 1$) to unit. In addition, CPI (ratio even-to-odd) for *n*-alkanoic acids can also be used to investigate their origin (Gogou et al., 1996).

- (c) Diagnostic concentration ratios of PAHs have been used to identify their emission sources (Grimmer et al., 1983; Sicre et al., 1987; Rogge et al., 1993a, b, d).

The ratio of the sum of concentrations of nine non-alkylated PAH (fluoranthene, pyrene, benz[a]anthracene, chrysene, benzoflouranthenes, benzo[e]pyrene, benzo[a]pyrene, indeno[cd]pyrene, and benzo[ghi]perylene) to the total concentration of PAH (CPAHs/TPAHs) has often been used as a characteristic diagnostic parameter for PAHs emitted from stationary combustion sources (Takada et al., 1990; Gogou et al., 1996). The MePh to Ph ratio (MePh/Ph) is used to characterize PAH emissions from mobile sources (exhaust emissions).

- (d) Cluster analysis was performed using the 1-Pearson *r* similarity method and the pair-group average linkage technique by means of the Statistical software package. The concentrations of each species of each sample were standardized (average 0, standard deviation 1) using the *Z*-score

$$Z_{ij} = \frac{C_{ij} - \bar{C}_i}{(\text{STDEV})_i},$$

where *i* is the number of analyzed elements, *j* is the number of the samples, Z_{ij} is the standardized value of the element *i* for the *j* sample, C_{ij} is the concentration of the element *i* for the *j* sample, \bar{C}_i is the average concentration of the element *i* and $(\text{STDEV})_i$ is the standard deviation of the *i* element concentration distribution.

4. Results and discussion

4.1. Organic compounds concentration levels and source reconciliation

Table 1 presents the following parameters: mean total concentration (and standard deviation) for each compound class; the homologue range ($C_n - C_m$) and the homologue with the highest concentration (C_{max}) for each compound class; diagnostic molecular parameters such as CPI for *n*-alkanes and *n*-alkanoic acids, wax *n*-alkanes content (%WAX) and UCM for aliphatic compounds. Table 1 also reports concentration ranges and diagnostic concentration ratios (Grimmer et al., 1983; Sicre et al., 1987; Gogou et al., 1996) for polycyclic aromatic hydrocarbons (PAHs) and oxygenated polynuclear aromatic compounds (O-PACs). Table 2 gives the mean concentration (and standard deviation) for individual homologues of *n*-alkanes, *n*-alkenes and isoprenoid hydrocarbons. The corresponding values for PAHs and O-PACs are reported in Table 3. The carboxylic acid mean concentrations and standard deviation are reported in Table 4.

4.1.1. Aliphatic compound and olefins

The aliphatic fraction of the analyzed organic aerosol was composed of *n*-alkanes, *n*-alk-1-enes, isoprenoid hydrocarbons and the mixture of cyclic, branched and unsaturated hydrocarbons (UCM) (Tables 1 and 2). *n*-Alkane homologues, from *n*-tetradecane (C_{14}) to *n*-pentatriacontane (C_{35}), were detected in both Santiago (August and October samples) and Temuco (September samples) (Table 1). A two-mode concentration pattern with maxima at *n*-hexadecane (C_{16} ; 36.1 ng m^{-3}) and *n*-tetracosane (C_{24} ; 18.0 ng m^{-3}) was observed for samples collected in Santiago in August (Table 2). A similar concentration pattern was observed for September samples in Temuco, (C_{16} ; 65.5 ng m^{-3}) and *n*-docosane (C_{22} ; 12.9 ng m^{-3}) (Table 2). Finally, a concentration pattern with a maximum at *n*-hexadecane (C_{16} ; 51.8 ng m^{-3}) was observed for *n*-alkanes in Santiago for the October samples (Table 2). The above-observed concentration profiles are indicative of the predominance of anthropogenic emissions (Simoneit et al., 1990; Gogou et al., 1996).

Mean total concentration of *n*-alkanes in Santiago in August ($282.8 (158.8) \text{ ng m}^{-3}$; Table 1) was slightly higher than that measured in the same area in October ($261.7 (81.3) \text{ ng m}^{-3}$; Table 1), and in Temuco in September ($257.9 (89.1) \text{ ng m}^{-3}$; Table 1). These concentrations are lower than those measured at Plaza Gotuzo (central Santiago) in 1991 (5400 ng m^{-3} ; Didyk et al., 2000). This significant difference might be explained by: (a) the use of a conventional high-volume collection system by Didyk et al. (2000) in comparison to this collecting only $\text{PM}_{2.5}$ in the present study; and

Table 1

Total concentration (ng m^{-3}) ranges and molecular diagnostic parameters of aliphatic, olefinic, aromatic and carboxylic compounds determined in $\text{PM}_{2.5}$ particles collected in Santiago and Temuco

	Santiago August 1998 $n = 9$	Temuco September 1998 $n = 6$	Santiago October 1998 $n = 4$
Aliphatic compounds			
<i>n-Alkanes</i>			
$(C_n - C_m); C_{\text{max}}$	$(C_{14} - C_{35}); C_{16}; C_{17}$	$(C_{14} - C_{35}); C_{17}$	$(C_{14} - C_{35}); C_{16}; C_{17}$
Total concentration (ng m^{-3})	282.8 (158.8)	257.9 (89.1)	261.7 (81.3)
CPI	0.79 (0.21)	0.43 (0.12)	1.00 (0.26)
% Wax	13.2 (7.5)	10.0 (4.0)	20.0 (8.3)
UCM (ng m^{-3})	838.9 (645.6)	343.6 (223.3)	1368.7 (731.4)
UCM/NA	3.8 (4.6)	1.2 (0.8)	4.9 (2.1)
<i>Isoprenoid hydrocarbons</i>			
Total concentration (ng m^{-3})	30.0 (25.4)	25.0 (10.4)	68.8 (25.5)
<i>n-Alk-1-enes</i>			
$(C_n - C_m); C_{\text{max}}$	—	$(C_{19} - C_{27}); C_{22}; C_{24}$	—
Total concentration (ng m^{-3})	—	16.1 (12.8)	—
Aromatic compounds			
<i>PAHs</i>			
Total concentration (ng m^{-3})	223.3 (168.4)	750.9 (304.3)	128.8 (134.6)
CPAHs/TPAHs	0.60 (0.17)	0.70 (0.04)	0.30 (0.10)
MePh/Ph	0.43 (0.25)	0.24 (0.06)	0.87 (0.50)
Fl/(Py + Fl)	0.45 (0.05)	0.57 (0.08)	0.47 (0.09)
BaA/(Ct + BaA)	0.27 (0.07)	0.41 (0.01)	0.45 (0.29)
BeP/(BaP + BeP)	0.60 (0.12)	0.41 (0.08)	0.65 (0.07)
IP/(IP + BgP)	0.28 (0.10)	0.47 (0.02)	0.29 (0.03)
<i>O-PACs</i>			
PAKs: total concentration (ng m^{-3})	0.7 (0.2)	3.8 (2.0)	1.0 (0.4)
PAQs: total concentration (ng m^{-3})	0.2 (0.1)	0.5 (0.4)	0.5 (0.4)
Carboxylic compounds			
<i>n-Alkanoic acids</i>			
$(C_n - C_m); C_{\text{max}}$	$(C_9 - C_{30}); C_{16}$	$(C_9 - C_{30}); C_{16}$	$(C_9 - C_{30}); C_{16}$
Conc. (ng m^{-3})	755.7 (347.6)	786.7 (260.2)	842.8 (161.7)
CPI	4.6 (2.3)	2.4 (0.8)	5.5 (2.4)
<i>n-Alkenoic acids</i>			
Total concentration (ng m^{-3})	110.5 (88.1)	166.3 (99.4)	603.5 (217.6)
<i>α,ω-dicarboxylic acids</i>			
Total concentration (ng m^{-3})	38.8 (23.2)	23.7 (15.2)	16.0 (7.3)

CPI: Carbon Preference Index, UCM: Unresolved Complex Mixture, NA: *n*-alkanes, %Wax: percentage of leaf wax *n*-alkanes in the total fraction of *n*-alkanes, CPAHs: combustion-derived PAHs, TPAHs: total PAHs, MePh/Ph: methyl-phenanthrene to phenanthrene, BA/BaA + 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).

(b) year to year changes of air quality. Higher $\text{PM}_{2.5}$ *n*-alkane concentrations ranging between 452.3 and 1439.1 ng m^{-3} were observed at the residential area of Las Condes by Kavouras et al. (1999a) in 1996. The higher concentration of *n*-alkanes at Las Condes might be due to air mass transport from central Santiago (McIver) to northern suburbs (Las Condes; located on the bottom of Andes), where airborne pollutants are

concentrated because of the temperature inversion layers (Oyola et al., 2000).

The CPI ($C_{14} - C_{35}$) of *n*-alkanes in Santiago ranged from 0.79 (0.21) up to 1.00 (0.26) (Table 1) and was 0.43 (0.12) (Table 1) in Temuco. These values are characteristic of fossil-fuels-related emissions. The low odd-to-even predominance for the entire range of *n*-alkanes (CPI < 1) in both urban areas, in conjunction with their

Table 2
Concentration (ng m^{-3}) of individual homologues of *n*-alkanes, *n*-alk-1-enes and isoprenoid hydrocarbons determined in $\text{PM}_{2.5}$ particles collected in Santiago and Temuco

	Santiago August 1998		Temuco September 1998		Santiago October 1998	
	Mean ^a	σ^a	Mean	σ	Mean	σ
<i>n</i> -Alkanes (ng m^{-3})						
C ₁₄	8.6	9.9	5.7	0.8	4.9	15.7
C ₁₅	14.6	19.0	16.0	21.4	8.3	10.9
C ₁₆	36.1	31.5	65.5	49.0	51.8	17.3
C ₁₇	21.9	13.3	18.5	6.2	30.9	15.9
C ₁₈	32.5	22.7	47.7	16.8	28.4	24.6
C ₁₉	10.0	4.9	6.3	2.2	20.6	6.9
C ₂₀	14.3	5.9	12.3	2.6	15.0	5.7
C ₂₁	9.8	2.9	9.6	2.9	13.1	4.7
C ₂₂	14.8	7.1	12.9	4.1	13.4	5.5
C ₂₃	14.7	6.7	10.8	4.3	8.3	2.3
C ₂₄	18.0	10.3	10.2	4.9	7.0	2.5
C ₂₅	15.0	12.3	8.5	5.1	6.2	2.4
C ₂₆	13.5	13.2	6.6	4.3	4.1	2.0
C ₂₇	12.6	13.5	6.3	4.7	4.9	1.6
C ₂₈	12.5	11.8	4.8	4.0	3.1	1.3
C ₂₉	10.2	8.9	5.4	4.1	4.9	1.0
C ₃₀	7.1	6.5	3.9	3.7	2.2	0.6
C ₃₁	7.2	6.0	4.2	4.4	3.0	0.4
C ₃₂	4.1	4.7	2.6	3.7	1.0	0.8
C ₃₃	3.2	4.0	2.4	4.4	0.4	0.5
C ₃₄	1.4	2.5	1.4	3.3	0.0	0.0
C ₃₅	0.8	1.5	0.7	1.6	0.0	0.0
<i>n</i> -Alkenes (ng m^{-3})						
C _{19:1}	ND ^b	ND	0.7	0.6	ND	ND
C _{20:1}	ND	ND	0.7	0.5	ND	ND
C _{21:1}	ND	ND	1.8	0.3	ND	ND
C _{22:1}	ND	ND	4.7	3.4	ND	ND
C _{23:1}	ND	ND	2.9	2.3	ND	ND
C _{24:1}	ND	ND	5.4	5.2	ND	ND
C _{25:1}	ND	ND	1.7	1.1	ND	ND
C _{26:1}	ND	ND	2.0	1.8	ND	ND
C _{27:1}	ND	ND	0.3	0.2	ND	ND
<i>Isoprenoid hydrocarbons</i> (ng m^{-3})						
Pr	14.3	12.7	9.4	4.5	39.2	12.7
Ph	15.7	12.7	15.6	6.0	29.7	12.7

^a Mean: mean concentration; σ : standard deviation.

^b ND: not detected.

low “wax” content (%Wax from 13.2 (7.5) up to 20.0 (8.3) in Santiago and 10.0 (4.0) in Temuco; Table 1) suggested that the concentrations observed in these two urban areas of Chile are mostly associated with human activities.

Organic compounds that can be used as tracers of organic aerosol sources (Simoneit, 1984, 1999) were also measured. Pristane and phytane, both tracers of oil residues, were detected in all $\text{PM}_{2.5}$ samples. The mean concentration of both pristane and phytane in Santiago

(30.0 (25.0) ng m^{-3} in August and 68.8 (25.5) ng m^{-3} in October; Table 2) was considerably higher than the corresponding concentration measured in Temuco (25.0 (10.4) ng m^{-3} ; Table 2). The hump observed in the aliphatic fraction chromatogram base line is indicative of the presence of a non-resolved mixture of branched, cyclic and unsaturated aliphatic hydrocarbons (Unresolved Complex Mixture, UCM; Gogou et al., 1996). High UCM concentrations observed in Santiago (838.9 (645.6) ng m^{-3} in August and 1368.7 (731.4) ng m^{-3} in

Table 3

Concentration (ng m^{-3}) of polycyclic aromatic hydrocarbons (PAHs) and oxygenated polynuclear aromatic compounds (O-PACs) determined in $\text{PM}_{2.5}$ particles collected in Santiago and Temuco

	Santiago August 1998		Temuco September 1998		Santiago October 1998	
	Mean ^a	σ^a	Mean	σ	Mean	σ
Polynuclear aromatic hydrocarbons (PAHs) (ng m^{-3})						
Fluorene	15.8	14.5	27.2	6.0	14.0	15.5
Phenanthrene	28.0	22.0	50.6	14.7	44.7	66.4
Anthracene	3.1	3.7	6.7	2.1	6.9	9.4
Me-Phenanthrenes	8.6	7.1	12.3	3.8	19.5	16.3
Dimethyl-phenanthrenes	6.7	4.2	5.6	1.4	5.4	2.9
Fluoranthrene	7.2	4.8	18.9	5.6	5.3	6.5
Pyrene	8.4	5.9	15.5	8.5	8.1	12.4
Methyl-Pyrenes/Fluoranthenes	4.5	3.9	21.6	11.1	2.6	2.7
Benzo[a]anthracene	8.5	5.6	115.7	44.3	1.2	0.8
Chrysene/Triphenylene	28.3	23.2	163.2	62.0	2.2	2.4
Benzo[b/j/k]fluoranthrene	36.4	31.6	98.5	31.8	3.3	1.9
Benzo[c]pyrene	20.3	18.2	73.0	36.4	3.2	2.0
Benzo[a]pyrene	10.9	8.1	98.5	38.3	1.8	1.0
Perylene	7.0	13.7	16.8	5.5	0.4	0.2
Anthranthrene	4.4	3.1	23.9	8.1	1.0	0.7
Indeno[1,2,3-cd]pyrene	9.7	7.3	68.8	22.2	2.4	1.5
Benzo[ghi]perylene	37.8	37.1	75.8	19.8	5.7	3.5
Coronene	5.8	6.3	8.4	2.1	0.9	0.8
Oxygenated polynuclear aromatic compounds (O-PACs)						
<i>Polynuclear aromatic quinones (PAQs) (pg m^{-3})</i>						
1,4 Naphthaquinone	14.4	30.8	7.2	17.6	61.6	123.2
9–10 Phenanthrenedione	9.7	4.7	24.3	31.9	15.8	31.5
1-Acenaphthoquinone	13.7	15.5	18.2	11.3	79.5	133.4
9–10 Anthracenedione	116.2	129.3	237.7	146.7	330.8	295.8
5–12 Naphthacenedione	36.5	32.9	247.3	459.7	13.1	26.3
<i>Polynuclear aromatic ketones (PAKs) (pg m^{-3})</i>						
9-Fluorenone	284.2	431.8	1550.5	1190.5	909.8	367.8
OPAH-254 6H-Benzo[cd]pyrene-6-one	127.8	123.8	282.2	210.5	ND	ND
OPAH-230 (benzathrone)	28.1	62.0	726.4	1197.2	31.7	53.2
OPAH-230 (benzathrone)	86.9	145.5	315.2	333.3	16.5	22.8
7H-Benzo[de]anthracene-7-one	119.5	111.4	702.3	718.5	39.9	79.9
4H-Cyclopenta[def]phenanthren-4-one	32.6	19.4	265.4	130.6	38.6	26.7
<i>Other O-PACs (pg m^{-3})</i>						
1,8 Naphthalic anhydride	ND ^b	ND	8.7	14.3	1.7	3.4
2-hydroxy-9-fluorenone	ND	ND	5.6	13.8	ND	ND

^a Mean: mean concentration; σ : standard deviation.

^b ND: not detected.

October; Table 1) and Temuco (343.6 (223.3) ng m^{-3} ; Table 1) suggested intense emissions from the incomplete wood, coal and fossil fuels combustion emissions (Sicre et al., 1987; Gough and Rowland, 1990). The mean UCM to *n*-alkanes (UCM/NA) concentration ratio in Santiago (3.8 (4.6) in August and 4.9 (2.1) in October; Table 1) was comparable to that previously reported for fossil fuel combustion emissions (Gogou

et al., 1996). In contrast, Temuco samples exhibited a low UCM/NA ratio (1.2 (0.8); Table 1), suggesting a lower petrogenic contribution to $\text{PM}_{2.5}$ aliphatic hydrocarbons. However, since both CPI and %Wax content values were low, direct emissions from higher terrestrial plants and vegetation debris may not be the predominant sources of aliphatic hydrocarbons in Temuco.

Table 4

Concentration (ng m^{-3}) of individual homologues of *n*-alkanoic, *n*-alkenoic, dicarboxylic and oxo-carboxylic acids determined in $\text{PM}_{2.5}$ particles collected in Santiago and Temuco

	Santiago August 1998		Temuco September 1998		Santiago October 1998	
	Mean ^a	σ^a	Mean	σ	Mean	σ
<i>n</i> -Alkanoic acids (ng m^{-3})						
C ₉	38.4	28.4	48.6	52.9	50.8	3.0
C ₁₀	74.0	65.4	56.1	64.8	60.5	6.1
C ₁₁	26.1	17.8	27.2	15.3	21.2	8.5
C ₁₂	32.2	24.5	23.2	15.7	19.5	5.3
C ₁₃	13.0	7.7	43.0	37.4	40.2	4.0
C ₁₄	38.1	67.2	112.4	141.5	127.0	20.6
C ₁₅	23.1	13.1	38.1	16.1	27.1	15.6
C ₁₆	280.9	130.1	175.0	85.3	130.1	63.4
C ₁₇	22.9	10.5	26.4	17.0	21.7	6.7
C ₁₈	93.6	47.6	45.5	22.7	34.1	16.1
C ₁₉	6.8	8.8	17.0	15.2	16.1	1.3
C ₂₀	13.8	6.2	23.0	14.0	18.5	6.3
C ₂₁	4.8	3.4	16.5	15.8	16.1	0.5
C ₂₂	35.3	19.5	74.9	37.5	56.2	26.4
C ₂₃	8.7	7.5	15.2	6.3	10.8	6.3
C ₂₄	10.2	7.2	14.4	3.4	8.9	7.7
C ₂₅	5.5	3.6	11.7	10.0	10.9	1.2
C ₂₆	6.6	4.4	7.8	5.2	6.5	1.8
C ₂₇	1.3	1.3	0.3	0.4	0.3	0.0
C ₂₈	12.9	9.4	8.5	8.5	8.5	0.0
C ₂₉	7.6	7.6	1.9	1.5	1.7	0.3
<i>n</i> -Alkenoic acids (ng m^{-3})						
C _{16:1}	33.7	47.5	59.4	53.4	56.4	4.2
C _{18:2}	10.2	7.2	32.4	18.1	25.2	10.1
C _{18:1}	66.6	43.9	74.5	52.8	63.7	15.4
Dicarboxylic and oxo-acids (ng m^{-3})						
dicC ₆	1.5	2.0	1.6	0.7	1.2	0.6
dicC ₈	2.2	2.3	2.3	1.7	2.0	0.4
dicC ₉	27.6	14.1	14.2	10.8	12.5	2.4
dicC ₂₂	7.5	7.3	5.6	2.6	4.1	2.1
oxo-C ₉	1.4	1.2	1.1	1.3	1.2	0.2
oxo-C ₈	1.1	0.9	2.3	1.3	1.8	0.7

^a Mean: mean concentration; σ : standard deviation.

n-Alk-1-enes were detected only in Temuco samples (Tables 1 and 2). In particular, olefins, from *n*-nonadec-1-ene (*n*-C_{19:1}) to *n*-heptacos-1-ene (*n*-C_{27:1}), with a mean total concentration of 16.1 (12.8) ng m^{-3} (Table 1) were identified. As shown in Table 2, *n*-docos-1-ene (*n*-C_{22:1}) and *n*-tetracos-1-ene (*n*-C_{24:1}) were the most abundant species of this compound group. These olefinic compounds are formed, during wood burning, through the dehydration of *n*-alkanols and decarboxylation of *n*-alkanoic acids present in the lipid pool such as lignins and celluloses (Simoneit et al., 2000). The concentration profile of *n*-alk-1-enes homologues observed in this study (Table 2) was similar to that reported for wood

burning (Simoneit et al., 2000; Abas et al., 1995). Thus, their presence can be attributed to wood burning, which is widely used in Temuco. In conclusion, petrogenic fuel related emissions were important sources of aliphatic hydrocarbons in both cities, as suggested the determined concentration diagnostic ratios and molecular tracers occurrence. Finally, wood burning was found to be an important source of $\text{PM}_{2.5}$ aliphatic hydrocarbons only in Temuco.

4.1.2. Polycyclic aromatic compounds

A series of parent and substituted polynuclear aromatic hydrocarbons from fluorene (166 g mol^{-1}) to

coronene (300 g mol^{-1}) was detected in all $\text{PM}_{2.5}$ samples (Table 3). Concentration differences were observed between the two urban areas. Similar compound concentrations were observed for petrogenic (phenanthrene, methylated phenanthrenes and pyrene) and pyrogenic (chrysene, benzofluoranthenes and benzo[ghi]perylene) PAHs in Santiago in August (Table 3). A strong predominance of low molecular weight petrogenic PAHs was observed in the same location in October (Table 3). In Temuco, high molecular weight PAHs including benzo[a]anthracene, chrysene, benzofluoranthenes and benzo[a]pyrene were the most abundant species of the measured aromatic fraction (Table 3).

August mean total PAH concentration in Santiago ($223.3 (168.4) \text{ ng m}^{-3}$; Table 1) was two times higher than the corresponding October concentration ($128.8 (134.6) \text{ ng m}^{-3}$; Table 1). This difference may be due to higher emissions of PAHs from combustion-related stationary sources in August (winter period). Higher concentrations (1003 ng m^{-3}) of total particulate PAHs have been reported for central Santiago (Didyk et al., 2000). This difference might be explained by: (a) the use of a conventional high-volume collection system by Didyk et al. (2000) in comparison to this collecting only $\text{PM}_{2.5}$ in our study. Although Temuco is a smaller city than Santiago, the mean total PAH concentration was notably higher ($750.9 (304.3) \text{ ng m}^{-3}$; Table 1) because of the wood burning in Temuco. Wood stoves are considered to be an important source of PAHs (Cooper, 1980).

To investigate the compositional differences between the two urban areas, PAHs concentration diagnostic ratios were calculated (Table 1). These ratios should be used with caution because PAHs are emitted from a variety of sources and their profiles can be altered due to their reactivity. The diagnostic ratio analysis (Table 1) suggested that PAHs were associated with several sources. The mean value of the sum of nine combustion-related non-alkylated compounds to the total concentration of PAHs (CPAHs/TPAH) was calculated (Gogou et al., 1996). The respective values were $0.30 (0.10)–0.60 (0.17)$ in Santiago and $0.70 (0.04)$ in Temuco (Table 1). The higher ratio values observed, suggested that a large fraction of PAH originated from combustion sources such as domestic heaters (Rogge et al., 1993a, b; McDonald et al., 2000). The methyl-phenanthrene to phenanthrene ratio (MePh/Ph) can be used to investigate the origin of PAHs, since a ratio > 1 indicates petrogenic sources (e.g. vehicular exhausts; Rogge et al., 1993a, b). The mean MePh/Ph ratio values were $0.43 (0.25)–0.87 (0.50)$ in Santiago and $0.24 (0.06)$ in Temuco (Table 1). The MePh/Ph ratio values obtained indicate that PAHs originate mostly from stationary combustion sources (Rogge et al., 1993a, b), especially in Temuco. The mean $[\text{Fl}/(\text{Fl} + \text{Py})]$ ratio was

$0.45 (0.05)–0.47 (0.09)$ in Santiago and $0.57 (0.08)$ in Temuco (Table 1). These values are similar to those previously reported for automobile and heavy truck emissions (Rogge et al., 1993a, b). $[\text{BaA}/(\text{BaA} + \text{CT})]$ ratio mean values ($0.27 (0.07)–0.45 (0.29)$ for Santiago and $0.41 (0.01)$ for Temuco; Table 1) are also similar to those calculated for oil combustion sources such as industrial emissions and heavy trucks (Rogge et al., 1993a, b). The mean $[\text{BeP}/(\text{BeP} + \text{BaP})]$ ratio values measured in Santiago ($0.60 (0.12)–0.65 (0.07)$; Table 1) were higher than the corresponding for Temuco ($0.41 (0.08)$; Table 1). Benzo[e]pyrene and benzo[a]pyrene are emitted from combustion sources at almost equal amounts. Since benzo[a]pyrene decays faster in the atmosphere than benzo[e]pyrene, this ratio has been used as an indicator of the lifetime of the organic aerosol in the atmosphere. Freshly emitted PAHs should have a $[\text{BeP}/(\text{BeP} + \text{BaP})]$ ratio equal to 0.50 (Grimmer et al., 1983). The $[\text{BeP}/(\text{BeP} + \text{BaP})]$ ratios (Table 1) suggest more aged combustion emissions in Santiago than in Temuco. The indeno[1,2,3-cd]pyrene to benzo[ghi]perylene (IP/(IP + BgP)) mean concentration ratios were $0.28 (0.10)–0.29 (0.03)$ in Santiago (Table 1). These values are lower than those calculated for Temuco ($0.47 (0.02)$; Table 1). A comparison of these values to those previously reported (0.18 for cars, 0.37 for diesel and 0.56 for coal; Grimmer et al., 1983) underlines the importance of mobile sources in Santiago and stationary sources (including wood and coal domestic heating) in Temuco. Overall the PAHs concentration diagnostic ratios estimated for Santiago suggest that PAHs are associated with a variety of stationary and mobile (e.g. vehicular) sources, whereas wood/coal combustion is mostly responsible for the elevated PAH concentrations observed in Temuco. This conclusion is further supported by the characteristic chromatographic profile of dimethyl- and ethyl-phenanthrenes (DMPs) (Figs. 1A and B). This chromatograph was used in order to investigate the contribution of fossil fuel and wood combustion emissions (Benner et al., 1996). The concentration pattern of DMPs depends on the combustion material and the temperature (Benner et al., 1996). Higher concentration of 2,6-DMP (No. 2), 1,3-, 2,10-, 3,9-, 3,10- DMP (No. 4) and 1,6-, 2,9- DMP (No. 5) (Figs. 1A and B) were measured for diesel particles (Benner et al., 1996). Wood combustion contribution exhibits high concentrations of the 1,7-DMP (No. 6) (Benner et al., 1996). The concentration profile of dimethyl-phenanthrenes in Santiago (Fig. 1A) is quite similar to that observed for diesel particles. This observation underlines the contribution of fossil fuel combustion and residues in Santiago. The concentration profile of dimethyl-phenanthrenes observed in Temuco (Fig. 1B), where 1,7-DMP (No. 6) is very abundant, indicated that diesel and wood combustion are important sources of this compound class.

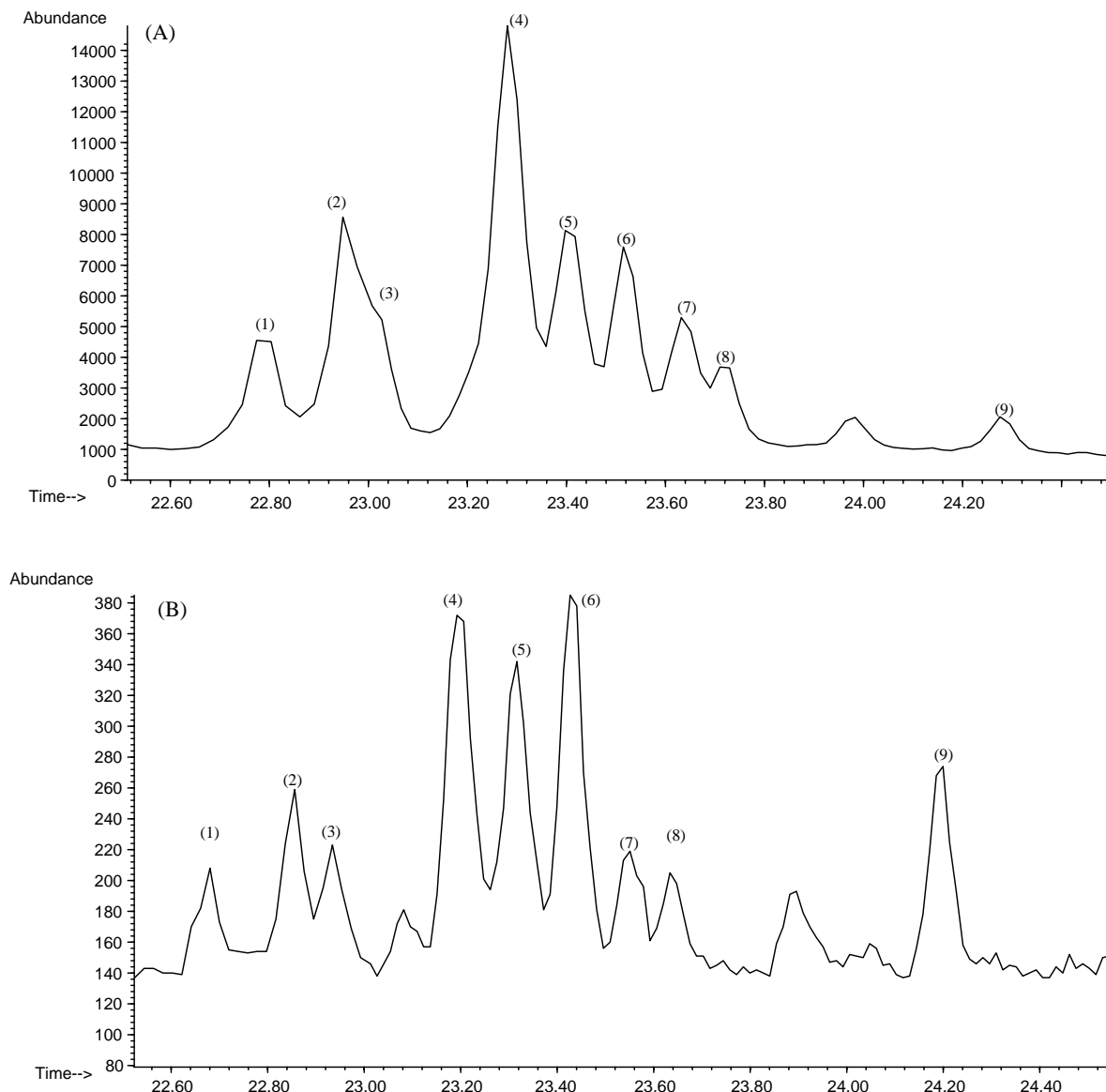


Fig. 1. Characteristic gas chromatogram of dimethyl-phenanthrenes (DMP; $m/z = 206$) in $PM_{2.5}$ particles collected in Santiago (A) and Temuco (B). (A and B: (1) 3,6 DMP; (2) 2,6 DMP; (3) 2,7 DMP; (4) 1,3/2,10/3,9/3,10 DMP; (5) 1,6/2,9 DMP; (6) 1,7 DMP; (7) 2,3 DMP; (8) 1,9/4,9 DMP; (9) 1,8 DMP.)

Oxygenated polynuclear aromatic compounds (O-PACs) are produced through photo-oxidation reactions of PAHs with atmospheric oxidants, including ozone and nitrogen oxides (Finlayson-Pitts and Pitts, 1997). In addition, O-PACs have been found in road dust, brake lining wear particles, and particulate exhaust emissions from heavy duty diesel trucks (Rogge et al., 1993a, b; Enya et al., 1997). A series of oxygenated O-PACs such as polycyclic aromatic quinones (PAQs) and ketones (PAKs) (Fig. 2 and Tables 1 and 3) were detected in all

samples. 9-Fluorenone, 7H-benzo(de)anthracene-7-one and 6H-benzo(cd)pyrene-6-one were the most abundant compounds (Fig. 2 and Table 3). The mean total PAKs concentration in Temuco ($3.8 (2.0) \text{ ng m}^{-3}$; Table 1) was higher than that measured in Santiago ($0.7 (0.2)–1.0 (0.4) \text{ ng m}^{-3}$; Table 1). O-PACs are formed through the atmospheric reactions of PAHs, with ozone and OH radicals (Finlayson-Pitts and Pitts, 1997). Since PAHs concentration was higher in Temuco than in Santiago (Table 1) we should also expect higher concentrations

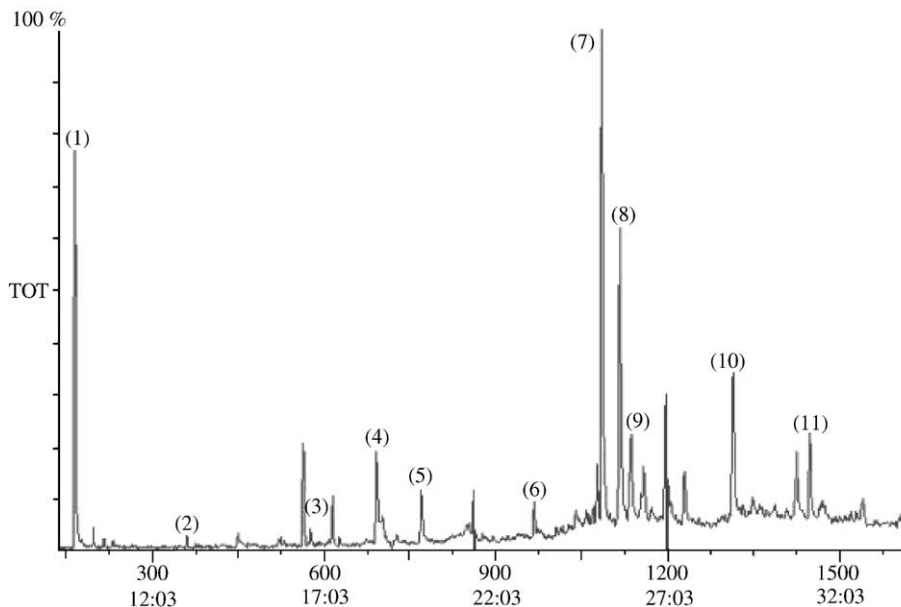


Fig. 2. Characteristic gas chromatogram of oxygenated polycyclic aromatic compounds (O-PACs) in $PM_{2.5}$ particles collected in Temuco: (1) IS (hexamethylbenzene); (2) 9-Fluorenone; (3) 1-Acenaphthenoquinone; (4) 9,10 Anthracenedione; (5) 4H-Cyclopenta[def]phenanthren-4-one; (6) 9,10 Phenanthrenedione; (7) 7H-Benzo[def]anthracene-7-one; (8) Benzathrone isomer; (9) Benzanthrone isomer; (10) 5,12 Naphthacenedione; (11) 6H-Benzo[cd]pyrene-6-one).

for their corresponding photochemical reaction products (e.g. PAKs) in Temuco (Table 1). In addition, since aromatic quinones are stable in the atmosphere, mean total PAQs concentrations were similar between the two urban areas (Temuco 0.5 (0.4) $ng\ m^{-3}$; Santiago 0.2 (0.1)– 0.5 (0.4) $ng\ m^{-3}$; Table 1).

4.1.3. Carboxylic acids

The acidic fraction was composed of *n*-alkanoic acids from nonanoic (C_9) to triacontanoic (C_{30}) acid, *n*-alkenoic acids, α,ω -dicarboxylic acids and ω -oxocarboxylic acids (Tables 1 and 4). Fatty acids, both saturated and unsaturated, originate from a wide variety of primarily natural sources (Gogou et al., 1996). Low molecular weight *n*-alkanoic acids, such as palmitic acid (C_{16}) and stearic acid (C_{18}) were the most abundant constituents in all samples (Table 4). Mean $PM_{2.5}$ *n*-alkanoic acids concentrations were similar in both urban areas (755.7 (347.6)– 842.8 (161.7) $ng\ m^{-3}$ in Santiago, and 786.7 (260.2) $ng\ m^{-3}$ in Temuco; Table 1). Mean CPI values for Santiago (4.6 (2.3)– 5.5 (2.4); Table 1) were similar to those observed in forested areas in Europe (Kavouras et al., 1999b, c), suggesting a biogenic origin of $PM_{2.5}$ associated alkanolic acids. However, mean CPI value in Temuco (2.4 (0.8); Table 1) samples, is hardly characteristic of natural sources (Simoneit, 1999). Although homologues $<C_{20}$ are primarily associated with microbial sources (Simoneit and Mazur-ek, 1982), they can also originate from anthropogenic

emissions including vehicle emissions, brake lining wears and paved road dusts (Simoneit, 1985; Rogge et al., 1993a, b).

n-Alkenoic acids are also emitted from the epicuticular waxes of higher terrestrial plants. In Santiago the mean concentration varied from 110.5 (88.1) up to 603.5 (217.6) $ng\ m^{-3}$ (Table 1). Palmitoleic ($C_{16:1}$), oleic ($C_{18:1}$) and linoleic ($C_{18:2}$) acids were detected in all samples. *n*-Alkenoic acids are very reactive under atmospheric conditions. Atmospheric oxidants (e.g. ozone) can attack the electron-rich double bond of unsaturated acids to form oxo- and dicarboxylic acids resulting to their presence in urban aerosols (Stephanou and Stratigakis, 1993). Furthermore, α,ω -dicarboxylic acids can also be associated with direct emissions from anthropogenic sources (Rogge et al., 1993a, b). Azelaic acid ($HOOC-(CH_2)_7-COOH$; dic C_9) was by far the most abundant compound of this subgroup (Table 4). Detectable amounts of succinic ($HOOC-(CH_2)_4-COOH$; dic C_6) and adipic ($HOOC-(CH_2)_6-COOH$; dic C_8) acids were also determined (Table 4). In addition, 8-oxo-nonanoic acid ($C(=O)-(CH_2)_6-COOH$; oxo- C_8) and 9-oxo-nonanoic acid ($C(=O)-(CH_2)_7-COOH$; oxo- C_9) were also determined (Table 4). These compounds are intermediate products of oleic acid ozone reactions (Stephanou and Stratigakis, 1993). Furthermore, α,ω - C_{22} was detected in both Santiago and Temuco samples. This compound is associated with natural sources such as microbial degradation and vegetation debris (Gogou et al., 1996).

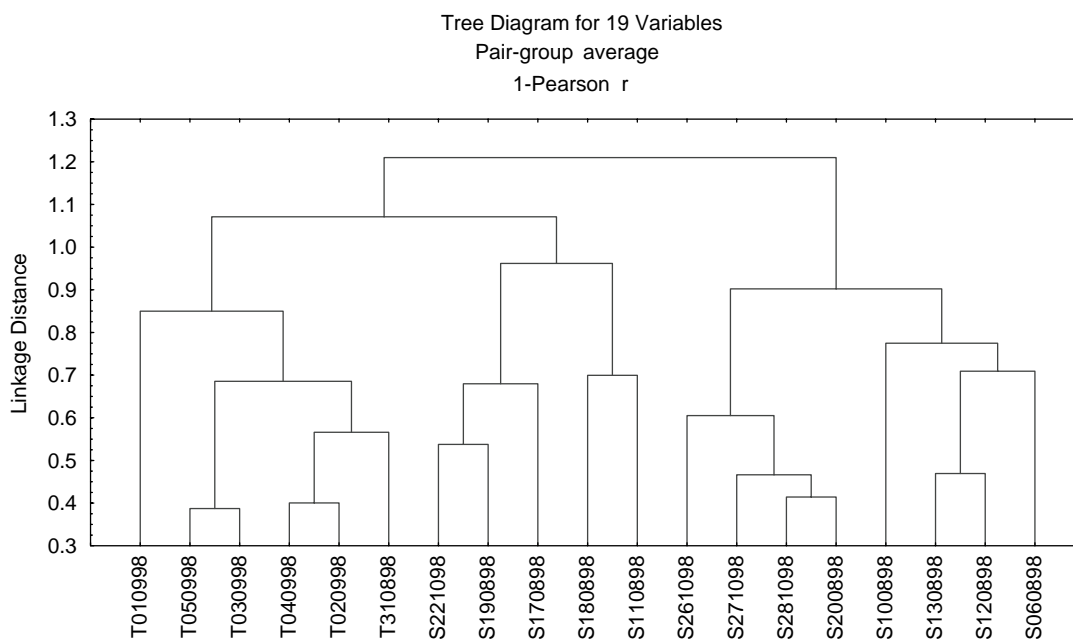


Fig. 3. Dendrogram of aerosol samples collected at Temuco (T) and Santiago (S) in corresponding dates (ddmmyy).

4.2. Cluster analysis results

Hierarchical cluster analysis is a complementary tool to molecular diagnostic ratios for the classification of the specific atmospheric conditions in respect of their sources. The measurement of the similarities or the dissimilarities in molecular composition of various atmospheric samples could be a useful indicator in order to identify the sources.

Cluster analysis technique was applied to the large spectrum of organic compounds (*n*-alkanes, *n*-alk-1-enes, polycyclic aromatic hydrocarbons (PAHs), oxygenated polycyclic aromatic compounds (O-PACs) and, *n*-alkanoic and *n*-alkenoic acids). Three major groups of samples were identified (Fig. 3). The first comprised the samples collected in Temuco. The other two comprised the samples collected in Santiago with no obvious pattern. The findings of cluster analysis confirmed the distinct difference in the organic aerosol composition between a large industrial urbanized area (Santiago) and a smaller city (Temuco) with no major industrial activities. These differences are in agreement with those obtained for the diagnostic ratio analysis.

5. Conclusions

PM_{2.5} samples were collected in two urban areas in Chile. The observed high UCM concentrations and the low CPI values (~ 1) suggested that gasoline and diesel-powered vehicles and trucks along with unburned fossil

fuels were the major sources of organic compounds in Santiago aerosol. Mobile combustion sources and domestic heating (including wood burning) were the most important sources of organic aerosols (especially PAHs), in Temuco aerosol. The detection of *n*-alk-1-enes and the chromatographic profile of dimethylphenanthrenes emphasized the contribution of wood burning to organic aerosol in Temuco. Furthermore, oxygenated PACs produced from photo-oxidation reactions of PAHs and emitted from combustion sources were also present in both cities. The concentration levels of all identified compounds were particularly high in both cities.

The compositional differences of organic aerosols between the two cities were also confirmed using cluster analysis.

Acknowledgements

The development and laboratory performance evaluation of the sampler was supported by US EPA STAR Grant No. R825 270-01-0. The Comisión Nacional del Medio Ambiente, Santiago de Chile, provided funding for the field measurements, under the Contract No. 07-0002-045. The support from the Research Account of the University of Crete (EPEAEK Program) is acknowledged. We also thank to Maritza Jadrijevic and Christian Santana for their personal engagement, to Jacqueline Peters for her fieldwork and to Rocío Toro for her local support at Temuco.

References

- Abas, M.R., Simoneit, B.R.T., Elias, V., Cabral, J.A., Cardoso, J.N., 1995. Composition of higher molecular weight organic matter in smoke aerosol from biomass combustion in Amazonia. *Chemosphere* 30, 995–1015.
- Artaxo, P., Oyola, P., Martinez, R., 1999. Aerosol composition and source apportionment in Santiago. *Nuclear Instrument and Methods in Physics Research B* 150, 409–416.
- Benner, B.A., Wise, S.A., Currie, L.A., Klouda, G.A., Klinedinst, D.B., Zweidinger, R.B., Stevens, R.K., Lewis, C.W., 1996. Distinguishing the contributions of residential wood combustion and mobile source emissions using relative concentrations of dimethylphenanthrene isomers. *Environmental Science and Technology* 29, 2382–2389.
- Bray, E.E., Evans, E.D., 1961. Distribution of n-paraffins as a clue to recognition of source beds. *Geochimica Cosmochimica Acta* 22, 2–15.
- Chow, J.C., Watson, J.G., Lowenthal, D.H., Solomon, P.A., Magliano, K.L., Ziman, S.D., Richards, L.W., 1993. PM₁₀ and PM_{2.5} compositions in California's San Joaquin Valley. *Aerosol Science and Technology* 18, 105–128.
- Chow, J.C., Watson, J.G., Fujita, E.M., Lu, Z.Q., Lawson, D.R., Ashbaugh, L.L., 1994. Temporal and spatial variations of PM_{2.5} and PM₁₀ aerosol in the Southern California Air Quality Study. *Atmospheric Environment* 28, 2061–2080.
- Cooper, J.A., 1980. Environmental impact of residential wood combustion emissions and its implications. *Journal of Air Pollution Control Association* 30, 855–861.
- Didyk, B.M., Simoneit, B.R.T., Pezoa, L.A., Riveros, M.L., Flores, A.A., 2000. Urban aerosol particles of Santiago, Chile: organic content and molecular characterization. *Atmospheric Environment* 34, 1167–1179.
- Eatough, D.J., Wadsworth, A., Eatough, D.A., Crawford, J.W., Hansen, L.D., Lewis, E.A., 1993. A multiple-system, multi-channel diffusion denuder sampler for the determination of fine-particulate organic material in the atmosphere. *Atmospheric Environment* 27A, 1213–1219.
- Enya, T., Suzuki, H., Watanabe, T., Hirayama, T., Hisamatsu, Y., 1997. 3-Nitrobenzanthrone, a powerful bacterial mutagen and suspected human carcinogen found in diesel exhaust and airborne particulates. *Environmental Science and Technology* 31, 2772–2776.
- Finlayson-Pitts, B., Pitts, J.N., 1997. Tropospheric air pollution: ozone, airborne toxics and polycyclic aromatic hydrocarbons and particles. *Science* 276, 1045–1051.
- Gough, M.A., Rowland, S.J., 1990. Characterization of unresolved complex mixtures of hydrocarbons in petroleum. *Nature* 344, 648–650.
- Gogou, A.I., Stratigakis, N., Kanakidou, M., Stephanou, E.G., 1996. Organic aerosols in Eastern Mediterranean: components source reconciliation by using molecular markers and atmospheric back trajectories. *Organic Geochemistry* 25, 79–96.
- Gogou, A.I., Apostolaki, M., Stephanou, E.G., 1998. Determination of organic molecular markers in marine aerosols and sediments: one step flash chromatography compound class fractionation and capillary gas chromatographic analysis. *Journal of Chromatography* 799, 215–231.
- Grimmer, G., Jacob, J., Naujack, K.W., 1983. Profile of the polycyclic aromatic compounds from crude oils-inventory by GC GC/MS. PAH in environmental materials: part 3. *Fresenius Zeitschrift fuer Analytische Chemie* 316, 29–36.
- Kavouras, I.G., Stratigakis, N., Stephanou, E.G., 1998a. Iso- and anteiso-Alkanes: specific tracers of environmental tobacco smoke in indoor and outdoor particle-size distributed urban aerosols. *Environmental Science and Technology* 32, 1369–1377.
- Kavouras, I.G., Mihalopoulos, N., Stephanou, E.G., 1998b. Formation of atmospheric particles from organic acids produced by forests. *Nature* 395, 683–686.
- Kavouras, I.G., Lawrence, J., Koutrakis, P., Stephanou, E.G., Oyola, P., 1999a. Measurement of particulate aliphatic and polynuclear aromatic hydrocarbons in Santiago: Source reconciliation and evaluation of sampling artifacts. *Atmospheric Environment* 33, 4977–4986.
- Kavouras, I.G., Mihalopoulos, N., Stephanou, E.G., 1999b. Formation and gas/particle partitioning of monoterpenes photo-oxidation products over forests. *Geophysical Research Letters* 26, 55–58.
- Kavouras, I.G., Mihalopoulos, N., Stephanou, E.G., 1999c. Secondary organic aerosol formation vs. primary organic aerosol emissions: in situ evidence for the chemical coupling between monoterpene acidic photo-oxidation products and new particle formation over forests. *Environmental Science and Technology* 7, 1028–1037.
- Kavouras, I.G., Koutrakis, P., Cereceda-Balic, F., Oyola, P., 2001a. Source apportionment of PM₁₀ and PM_{2.5} in five Chilean cities using factor analysis. *Journal of Air and Waste Management Association* 51, 451–464.
- Kavouras, I.G., Koutrakis, P., Tsapakis, E., Lagoudaki, E., Stephanou, E.G., von Baer, D., Oyola, P., 2001b. Source apportionment of urban particulate aliphatic and polynuclear aromatic hydrocarbons (PAHS) using multivariate methods. *Environmental Science and Technology* 35, 2288–2294.
- Kawamura, K., Gagosian, R.B., 1987. α,ω -Oxocarboxylic acids in the remote marine atmosphere: implication of photo-oxidation for unsaturated alkanic acids. *Nature* 325, 330–332.
- Koutrakis, P., Sioutas, C., Lawrence, J., 1998. Design and evaluation of a novel SVOC sampler: 1. Gas-phase diffusion denuder to trap organics. EPA Progress Report, Research Triangle Park, NC 27711.
- Mastral, A.M., Callen, M.S., 2000. A review on polycyclic aromatic hydrocarbon (PAH) emissions from energy generation. *Environmental Science and Technology* 34, 3051–3057.
- McDonald, R.D., Zielinska, B., Fujita, E.M., Sagebiel, J.C., Chow, J.C., Watson, J.G., 2000. Fine particle and gaseous emission rates from residential wood combustion. *Environmental Science and Technology* 34, 2080–2091.
- Nielsen, T., 1996. Traffic contribution of polycyclic aromatic hydrocarbons in the center of a large city. *Atmospheric Environment* 30, 3481–3490.
- Oros, D.R., Simoneit, B.R.T., 1999. Identification of molecular tracers in organic aerosols from temperate climate vegetation subjected to biomass burning. *Aerosol Science and Technology* 31, 433–445.
- Oyola, P., Martinez, R., Flores, V., Kavouras, I.G., Koutrakis, P., von Baer, D., Gidhagen, L., Artaxo, P., 2000. Measurement and trajectory analysis of PM_{2.5}, elemental and

- organic carbon in Santiago Metropolitan Region, Chile. Paper Presented in Seventh International Conference on Carbonaceous Particles in the Atmosphere, 26–29 November 2000, San Juan, Puerto Rico.
- Purvis, C.R., McCrillis, R.C., 2000. Fine particulate matter (PM) and organic speciation of fireplace emissions. *Environmental Science and Technology* 34, 1653–1658.
- Rogge, W.F., Hildemann, L., Mazurek, M.A., Cass, G.R., Simoneit, B.R.T., 1993a. Sources of fine organic aerosol: 2. Noncatalyst and catalyst-equipped automobiles and heavy duty diesel trucks. *Environmental Science and Technology* 27, 636–651.
- Rogge, W.F., Hildemann, L., Mazurek, M.A., Cass, G.R., Simoneit, B.R.T., 1993b. Sources of fine organic aerosol: 3. Road dust, tire debris and organometallic brake lining dust: roads as sources and sinks. *Environmental Science and Technology* 27, 1892–1904.
- Rogge, W.F., Hildemann, L., Mazurek, M.A., Cass, G.R., Simoneit, B.R.T., 1993c. Sources of fine organic aerosol: 5. Natural-gas home appliances. *Environmental Science and Technology* 27, 2736–2744.
- Rogge, W.F., Hildemann, L., Mazurek, M.A., Cass, G.R., Simoneit, B.R.T., 1993d. Sources of fine organic aerosol: 4. Particulate abrasion products from leaf surfaces of urban plants. *Environmental Science and Technology* 27, 2700–2711.
- Sicre, M.A., Marty, J.C., Saliot, A., Aparicio, X., Grimalt, J., Albaiges, J., 1987. Aliphatic and aromatic hydrocarbons in different sized aerosols over the Mediterranean Sea: occurrence and origin. *Atmospheric Environment* 21, 2247–2259.
- Simoneit, B.R.T., 1984. Application of molecular marker analysis to reconcile sources of carbonaceous particulates in tropospheric aerosols. *Science of the Total Environment* 36, 61–72.
- Simoneit, B.R.T., 1985. Application of molecular marker analysis to vehicular exhaust for source reconciliations. *International Journal of Environmental Analytical Chemistry* 22, 203–233.
- Simoneit, B.R.T., 1989. Organic matter of the troposphere—V. Application of the molecular marker analysis to biogenic emissions into the troposphere for source reconciliation. *Journal of Atmospheric Chemistry* 8, 251–275.
- Simoneit, B.R.T., 1999. A review of biomarker compounds as source indicators and tracers for air pollution. *Environmental Science and Pollution* 6, 159–169.
- Simoneit, B.R.T., Mazurek, M., 1982. Organic matter of the troposphere—II. Natural background of biogenic lipid matter in aerosols over the rural Western United States. *Atmospheric Environment* 16, 2139–2159.
- Simoneit, B.R.T., Cardoso, J.N., Robinson, N., 1990. An assessment of terrestrial higher molecular weight lipid compounds in aerosol particulate matter over the South Atlantic from about 30–70°S. *Chemosphere* 21, 1285–1301.
- Simoneit, B.R.T., Rogge, W.F., Lang, Q., Jaffe, R., 2000. Molecular characterization of smoke from campfire burning of pine wood (*Pinus elliottii*). *Chemosphere: Global Change Science* 2, 107–122.
- Stephanou, E.G., 1992. α,ω -Dicarboxylic acid salts and α,ω -dicarboxylic acids: photo-oxidation products of unsaturated fatty acids, present in marine aerosols and marine sediments. *Naturwissenschaften* 79, 128–131.
- Stephanou, E.G., Stratigakis, N., 1993. Oxocarboxylic and α,ω -dicarboxylic acids: photooxidation products of biogenic unsaturated fatty acids present in urban aerosols. *Environmental Science Technology* 27, 1403–1407.
- Takada, H., Onda, T., Ogura, N., 1990. Determination of polycyclic aromatic hydrocarbons in urban street dusts and their source materials by capillary gas chromatography. *Environmental Science and Technology* 24, 1179–1186.
- United States Environmental Protection Agency, March 2000. National air pollutants emission trends, 1900–1998, EPA-454/R-00-002. Office of Air Quality Planning and Standards, Research Triangle Park, NC.
- Zheng, M., Fang, M., Wang, F., To, K.L., 2000. Characterization of the solvent extractable organic compounds in PM_{2.5} aerosols in Hong Kong. *Atmospheric Environment* 34, 2691–2702.