# Estimations of primary and secondary organic carbon formation in PM$_{2.5}$ aerosols of Santiago City, Chile

Rodrigo Seguel A. [a], Raúl G.E. Morales S. [b,*], Manuel A. Leiva G. [a,b,**]

[a] Centro Nacional del Medio Ambiente (CENMA), Av. Larraín 9975, Santiago, Chile, CP 788-0096 La Reina
[b] Centro de Química Ambiental. Facultad de Ciencias, Universidad de Chile, Casilla 653, Santiago, Chile

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## ABSTRACT

High concentration of fine airborne particulates is considered one of the major environmental pollutants in Santiago, the Chilean Capital city, which in 1997 was declared a PM$_{10}$ saturated zone. To date there is no control of the amounts of fine and coarse aerosols concentrations and the source and chemical characterizations of the PM$_{2.5}$ particulates in the carbonaceous fractions are not well known even though this fraction could be represented almost the 50% in mass of the PM$_{2.5}$.

In this work, we present for the first time determinations of primary organic aerosol (POA) and secondary organic aerosol composition (SOA) fractions of the total mass of PM$_{2.5}$ particulates collected in the urban atmosphere of Santiago City. Our purpose is to know the anthropogenic contributions to the formation of SOA. To accomplish this we used the elemental carbon (EC) and organic carbon (OC) determinations developed by automatic monitoring stations installed in the city during the period 2002–2005, with a particular analysis of the summer time occurred in February 2004. Based on the EC tracer method, we have estimated the POA and SOA fraction and our data permit us to estimate the SOA reaching up to 20% of total organic aerosol matter, in good agreement to other measurements observed in large cities of Europe and U.S.A.

## 1. Introduction

Airborne particulate matter (PM) is one of the major pollutants in urban areas (Molina and Molina, 2004), in special the PM$_{2.5}$ fraction that corresponds to fine particles of 2.5 μm average aerodynamic diameter. It is well known that these particulates may cause serious health problems, currently associated with respiratory and cardiovascular diseases affecting the morbidity and mortality levels (Kampa and Castanas, 2008; Taus et al., 2008; Ballester et al., 2008; Lippmann, 2007). In recent years, several studies have shown the importance of PM$_{2.5}$ concentration in the evaluation of the air quality in large cities with high-density population and intense anthropogenic activities (Gurjar et al., 2008; Leiva et al., 2004; Fang et al., 2008). In Santiago, the Chilean capital city, with near six million inhabitants (INE, 2002), a program supported by the Air Quality Control Commission (CONAMA) to measure the concentration of PM$_{2.5}$ has been initiated recently. The purpose of this initiative is to prevent the impact of this pollutant on the population health (Cakmak et al., 2007; Cifuentes et al., 2001; Franklin and Schwartz, 2008).

Among the major components of PM$_{2.5}$ are the carbonaceous species, (Baltensperger et al., 2005; Leiva et al., 2005; Didyk et al., 2000; Morales et al., 1995) generated by chemical combustion processes in industrial and motor vehicles. These species can be characterized by the amounts of elemental carbon (EC) and organic carbon (OC) (Baltensperger et al., 2005; Baltensperger and Prevot, 2008; Barthelmie and Pryor, 1997; Lim and Turpin, 2002). EC is produced in the incomplete combustion of carbon-based materials and fuels and it is exclusively of primary nature. On the other hand, OC is directly emitted to the atmosphere from anthropogenic and biogenic sources and it is the basis of primary organic aerosols (POA). Organic carbon is also formed in the atmosphere from low-volatility products produced by the oxidation of gas-phase precursors and constitutes a major component of the secondary organic aerosol (SOA) (Alves and Pio, 2005; Moore et al., 2007; Wang et al., 2005). The direct determination of SOA is rather difficult, mainly because of the complexity of the OC reaction pathways, the vast number of products formed by photochemical and thermal oxidation reactions, and the cost involved in the analytical methods required for speciation. Nevertheless, it is possible to use an indirect method for

* Corresponding author. Tel.: +562 978 7170.
** Corresponding author. Tel.: +562 299 41 70.
E-mail addresses: raulgem@uchile.cl (R.G.E. Morales S.), manleiva@cenma.cl (M.A. Leiva G.).

quantitative assessment of secondary organic aerosols (SOA), as the EC trace method, which has become very useful (Chu, 2005; Chu et al., 2004; Lonati et al., 2005; Plaza et al., 2006; Turpin and Huntzicker, 1991; Turpin et al., 1991).

Santiago City ($33.5°$S, $70.6°$W) is located in a valley in the central zone of Chile, in between two rivers, Maipo and Mapocho, covering a surface of about 1400 square kilometers, 500 m above sea level, and surrounded by a ring of hills belonging to the Andes and the Coastal range mountains (Fig. 1). The weather in Santiago is Mediterranean type and its wind pattern is complex due to the topography and urban surface roughness. However, Santiago presents a very persistent valley–mountain breeze system with a predominant low speed wind direction from southwest, frequently lower than $2.0 \, \text{m s}^{-1}$ in autumn and winter. In addition to these physical characteristics, the prevailing anticyclonic meteorological conditions throughout the year, lead to a permanent subsidence and thermal inversion layer between 400 and 1000 m above the city, thus providing a very stable atmospheric gradient that reduces the dispersion of air pollutants (Morales, 2006; Jorquera et al., 2004). The urban atmosphere is a heavily PM-polluted environment, due to anthropogenic activities performed by almost six million peoples localized in an abrupt topographical valley, in the west side of the Andes mountain, and particularly in autumn and winter time because the Pacific anticyclone route (IGM, 1979; Morales, 2006). Due to these physical conditions, airborne particulate matter has been recognized as the major pollutant and the city was declared PM saturated by CONAMA (2004), including both modes, coarse and fine, whose concentrations are approximately in the ratio 1:1, according to recent studies (Koutrakis et al., 2005).

During summer time Santiago presents better ventilation conditions than in the winter period reaching the annual lowest PM concentrations. By the contrary, the greater solar irradiance together with an increase in $NO_x$ and Volatile Organic Compounds (VOC) determine a noteworthy rise in ozone levels (Rubio et al., 2006; Rappengluck et al., 2005). This has motivated us to estimate the concentrations of POA and SOA fractions with respect to the total OC, in order to characterize the main carbon components of the $PM_{2.5}$ fraction during summer time. Thus, the distinction of the carbonaceous matter between primary and secondary sources could have important implications for the adoption of a strategy for $PM_{2.5}$ mass concentrations control. Therefore, in this work we present the first attempts to quantify the relative contribution of carbonaceous species in $PM_{2.5}$ aerosols in the urban atmosphere of Santiago City. In addition, the presence of SOA has been evaluated by means of the EC trace model and using data collected by the air quality program administrated by the city government during the period 2002–2005.

## 2. Material and methods

### 2.1. Sampling sites and descriptions

Since 1997 Santiago Metropolitan Government established an Air Quality Pollution Watch Program, managed by the Ministry of Health. Eight monitoring stations distributed into the city are currently measuring concentrations of pollutant gases and atmospheric aerosols ($PM_{2.5}$), as well as, meteorological data. All these stations support the so-called MACAM-2 network, base of the Air Quality Monitoring Program in Santiago Metropolitan Area (Fig. 1 and Table 1). The eight monitoring stations determine $PM_{10}$, $O_3$, CO and $SO_2$, and only three of them determine $PM_{2.5}$: Las Condes (M label), Parque O'Higgins (N label), and Pudahuel (O label), see Fig. 1, while $NO_x$ is determined in the last two stations already mentioned.

### 2.2. Pollutant concentration measurement

The $PM_{2.5}$ concentrations were determined by means of a TEOM (Tapered Element Oscillating Microbalance) equipment, from Thermos Co., U.S.A., which provides data every 5 min at 50 °Celsius degrees. Data obtained since 2002 up to 2005 were previously validated for fix vacancies, duplicated entries and gaps by the National Committee for Environment at the Metropolitan Region
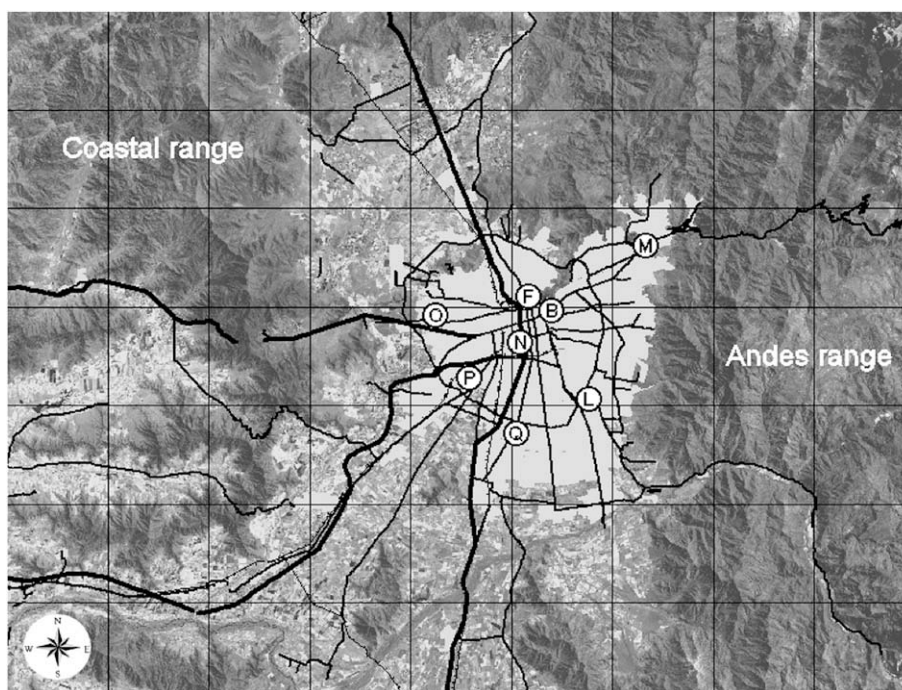


**Fig. 1.** Regional topography of the Santiago City, Chile (in a 10 km grid line). Grey area is the urban region and the black lines represent the main routes and streets. White dots designate the eighth air quality monitoring stations of the MACAM-2 network (M label: Las Condes, B label: Providencia, F label: La Paz, N label: Parque O'Higgins, L label: La Florida, O label: Pudahuel, P label: Cerrillos and Q label: El Bosque).

**Table 1**
Station locations of the MACAM-2 network at Santiago Metropolitan Area.

| Label[a] | Station | Latitude (S) | | | Longitude (W) | | | Altitude (m)[b] |
|---|---|---|---|---|---|---|---|---|
| B | Providencia | 33° | 25' | 59" | 70° | 37' | 29" | 590 |
| F | La Paz | 33° | 25' | 09" | 70° | 38' | 55" | 588 |
| L | La Florida | 33° | 30' | 48" | 70° | 35' | 09" | 654 |
| M[c] | Las Condes | 33° | 22' | 26" | 70° | 31' | 21" | 811 |
| N[c] | Parque O'Higgins | 33° | 27' | 40" | 70° | 39' | 29" | 562 |
| O[c] | Pudahuel | 33° | 26' | 06" | 70° | 44' | 52" | 553 |
| P | Cerrillos | 33° | 29' | 33" | 70° | 42' | 46" | 528 |
| Q | El Bosque | 33° | 32' | 38" | 70° | 39' | 50" | 574 |

[a] Labels are according to Fig. 1.
[b] Above sea level
[c] Stations selected for the present study.

(CONAMA-RM). Ozone was determined from Beckman equipment, model 950, while $NO_x$ determinations were done in a Monitor Labs Inc., ML9841A.

### 2.3. EC and OC measurements

Concentrations of OC and EC particulates were continuously determined by a thermal analysis method using ambient carbon particulate monitors, Model 5400 manufactured by Rupprecht and Patashnick Co. Inc (RPM5400). This instrument collects airborne particulate matter ($PM_{2.5}$) at a constant temperature of 50 °C and constant flow ($1 \, m^3 \, h^{-1}$) on an impactor plate with a 50% cut-off diameter of 0.14 μm. Next, a sequential oxidation is produced in a particle-free ambient air at different combinations of temperature, pyrolyze, and combust the carbon-containing compounds are then by nondispersive infrared $CO_2$ sensor. The $CO_2$ produced by the oxidation is analysed in situ and its concentration is related to carbon mass in temperature selectable organic aerosol fractions. The amounts of carbonaceous substances evolved at 340 °C were defined as OC and that at 750 °C as total carbon (TC), then, the difference between the amounts of TC and OC gives the amount of EC. The quality assurance and quality control program for this type of measurements consist in a check of the flow rate at the inlet with an audit flow meter and automatic leak check and $CO_2$ audit (zero and span) when bottled $N_2$ and $CO_2$ span gas are connected to the monitor. This performance is operated on a weekly basis.

The thermal method used to measure carbonaceous aerosols, RPM5400, is recognized as one of the best techniques (Cachier et al., 1989), but nevertheless, it faced negative artifact problems, caused by the incomplete collection of particles smaller than 0.14 μm and by the evaporation of organic gases (Matsumoto et al., 2003). As a result, the OC concentrations are underestimated while the EC are overestimated. This operating aspect should be considered at the time of interpreting the data because it was found that much of the variability depends on the type of measurement methods used. This problem still needs to be resolved (Jones and Harrison, 2005; Ren-Jian et al., 2007). Otherwise, the comparison between results obtained by the Aethalometer, an optical measurement method, and by RPM5400 (Artaxo et al., 1999) show good agreement and both instruments give confidence to measure black carbon concentration in urban aerosols.

### 2.4. EC tracer method

The SOA determination in the total OC concentration measured in a sampling site by means of the EC tracer method is based on the observation that background OC/EC ratios are smaller than OC/EC
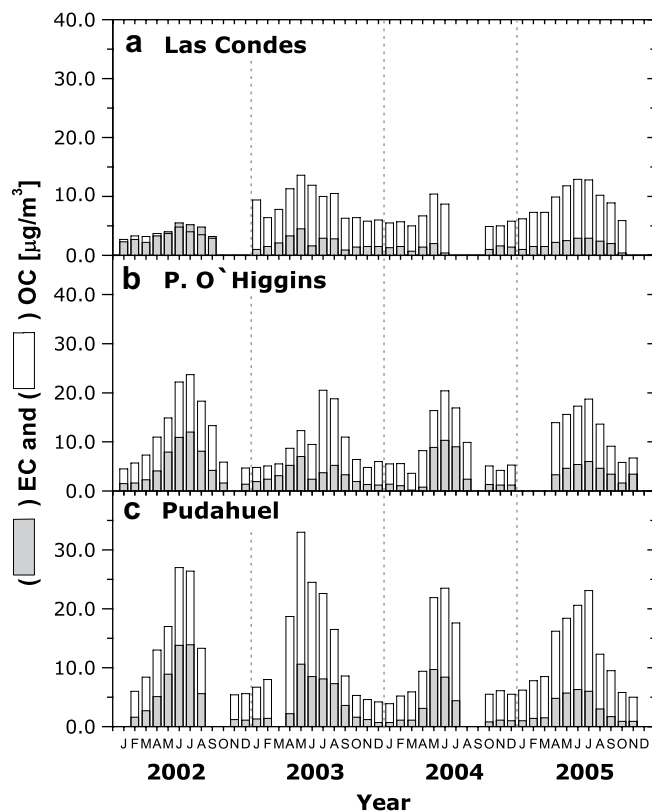


**Fig. 2.** Annual time series of the organic carbon (OC) and elemental carbon (EC) in $PM_{2.5}$ at (a) Las Condes (M label), (b) Parque O'Higgins (N label) and (c) Pudahuel (O label) stations. The stations labels are according to Fig. 1. Data source: Chilean Ministry of Health, Metropolitan area (SEREMI-RM).
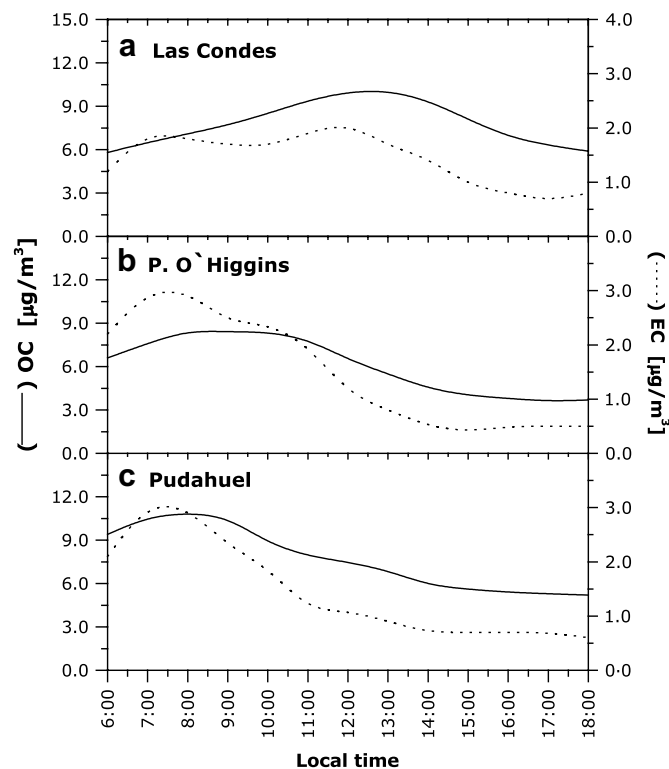


**Fig. 3.** Average Diurnal pattern of the organic carbon (OC; ––) and elemental carbon (EC; - - -) in $PM_{2.5}$ at (a) Las Condes (M label), (b) Parque O'Higgins (N label) and (c) Pudahuel (O label) in the February 2004. The stations labels are according to Fig. 1.
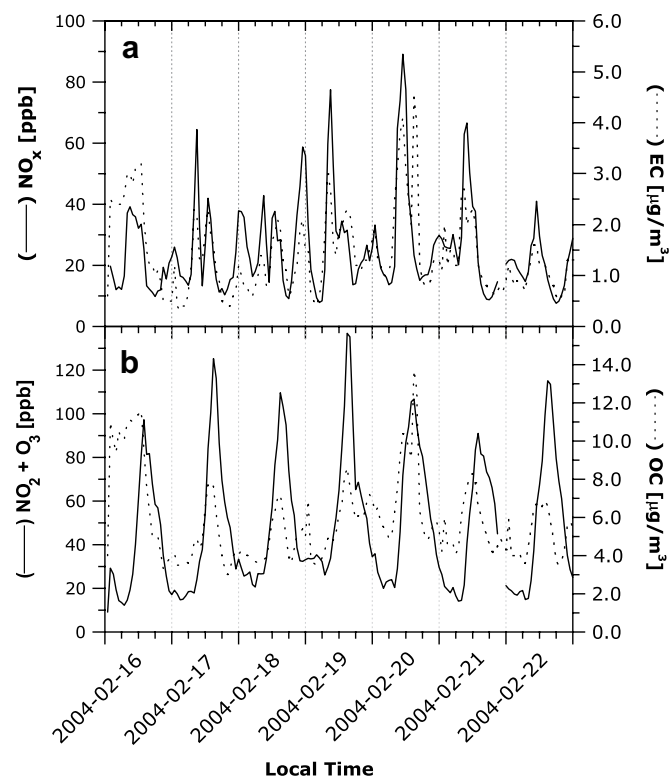
**Fig. 4.** Diurnal cycles of (a) $NO_x$ (––) compared with EC (- - -) in $PM_{2.5}$ and (b) $NO_2 + O_3$ (––) compared with OC (- - -) in $PM_{2.5}$ at Las Condes (M label) station in seven representative days of February 2004. See Fig. 1 for station label.

ratios found during peak photochemical periods (Duan et al., 2005; Viana et al., 2007). This is explained by the fact that EC, contrarily to primary OC, a precursor of secondary OC, is unaffected by photochemical oxidation reactions. Nevertheless, OC and EC emissions vary from source to source and hence the primary OC/EC ratio will be influenced by local sources, meteorological variables and by diurnal and seasonal fluctuations in emissions rates. Therefore, it is only possible to determine the OC/EC ratio when the photochemical activity is low, since at higher values the formation of SOA will increase the OC/EC ratio.

The SOA fraction in the $PM_{2.5}$ mass was estimated using EC as a tracer, assuming that primary organic carbon ($[OC]_p$) can be obtained from equation (1):

$$[OC]_p = \left[\frac{OC}{EC}\right]_p [EC] - b \tag{1}$$

In turns, the secondary organic carbon ($[OC]_s$) contribution to the total OC can be estimated as the difference between the total organic and primary carbon concentrations:

$$[OC]_s = [OC] - [OC]_p \tag{2}$$

Here, $[OC/EC]_p$ is the ratio of OC to EC for the primary sources in the site of interest, $b$ is the non-combustion contribution to the primary OC and sampling artefacts (Turpin and Huntzicker 1991; Lim and Turpin, 2002; Park et al., 2005), [EC] is the measured EC concentration and [OC] is the measured OC concentration. All of these parameters are time dependent because of the temporal variations in anthropogenic emissions and meteorology. Several methods are proposed in the literature to determine ($[OC/EC]_p$). In this work, we have decided to use the average ($[OC/EC]_p$) ratio and $b$ determined as constant factors in early morning (06.00–10.00 h.
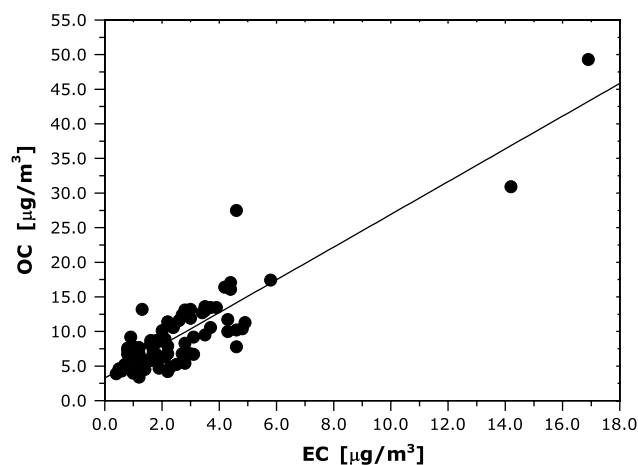


**Fig. 5.** Scatter plot of OC and EC in $PM_{2.5}$, corresponding to the hourly summer data pairs under low photochemical activity (06.00–10.00 h at local time), in the period of the February 2004 at Las Condes station (M Label in Fig. 1).

local time), when the solar radiation intensity is low. We have analyzed all the available data corresponding to the period from 2002 to 2005, choosing February 2004 to represent a monthly period due to the completeness of the data collected by the MACAM-2 network in summer.

## 3. Results and discussion

### 3.1. Seasonal, spatial and daily variation of EC and OC

Results of OC and EC monthly concentrations determined from the $PM_{2.5}$ particulates collected at three sampling sites from 2002 to 2005 are shown in Fig. 2. Seasonal fluctuations of EC and OC are clearly observed, showing that where autumn–winter concentrations (April–September) are higher than those recorded in spring–summer time (October–March). The large levels of OC and EC observed during autumn and winter seasons may be mainly explained by the prevalence of the Pacific anticyclonic meteorological conditions with a permanent subsidence and thermal inversion layer, mixing heights are around 400 m in winter time and around 1000 m in summer, in spite of the PM removal by wet scavenging in winter.

It is a well-known fact that the OC and EC concentrations can vary from place to place. Our results show that the highest mean OC and EC concentrations occur at Pudahuel station (Fig. 2c), localized in an urban site that is influenced by local primary emissions from nearby industrial, international airport and residential areas. On the other hand, the lowest mean OC and EC concentrations occur at Las Condes station (Fig. 2a), installed in an exclusively residential area.

Diurnal evolution of EC and OC was measured from the averaged hourly values in February 2004 and the results are shown in Fig. 3.

**Table 2**
OC/EC primary ratio ($[OC/EC]_p$), non-combustion contribution to the primary OC ($b$) in $\mu g\ m^{-3}$ and square of a correlation coefficient ($r^2$) according to EC tracer method (equations (1)) in $PM_{2.5}$ between 0.6.00 and 10.00 h in the period of the February 2004 at the station under study.

| Stations[a] | $[OC/EC]_p$ | $b$ ($\mu m^{-3}$) | $r^2$ |
|---|---|---|---|
| Las Condes (M) | 1.60 | 2.52 | 0.83 |
| Parque O'Higgins (N) | 1.56 | 4.12 | 0.59 |
| Pudahuel (O) | 1.56 | 3.78 | 0.77 |

[a] Labels are according to Fig. 1.

**Table 3**
Inorganic and Organic fractions average (in percentage) into the $PM_{2.5}$ masses in the period of the February 2004 at the station under study.

| Stations[a] | $PM_{2.5}$[b] ($\mu g\,m^{-3}$) | Inorganic fraction (IF%) | Carbon fraction (CF%) |
|---|---|---|---|
| Las Condes (M) | $31 \pm 13$ | 74 | 26 |
| Parque O'Higgins (N) | $33 \pm 15$ | 81 | 19 |
| Pudahuel (O) | $24 \pm 10$ | 78 | 22 |

[a] Labels are according to Fig. 1.
[b] Values represent average $\pm$ standard deviation.

An early morning peak (07.00–09.00 h) is clearly observed in the averaged EC concentrations in Pudahuel and Parque O'Higgins stations, probably due to local traffic. Instead, at Las Condes station a maximum emerges at middle day, associated to airborne material transported by wind, following the typical southwest predominant wind direction observed in the city, between 10.00 and 13.00 h. From 14:00 to 20:00 h at all stations EC values decreased to nocturnal values. On the other hand, while EC and OC concentrations follow a similar trend in Pudahuel and Parque O'Higgins stations, OC concentration does not follow the same pattern at Las Condes station, where a maximum could be observed just after the morning traffic peak in coincidence with the EC maximum observed between 10.00 and 13.00 h.

It is a well-known fact that in general there is a good correlation between $NO_x$ and EC due to primary character of both species, and revealing the non-photochemical source of the EC aerosol. In order to analyze the predominance of the primary and secondary source in the EC and OC species, we have correlated the hourly resolution of EC and OC measurements with the diurnal evolution of the concentrations of the $NO_x$ and $O_3$ gaseous species. This fact can be well appreciated in Fig. 4a corresponding to a selected week of the February 2004. On turn, the time evolution of $NO_2$ and $O_3$ gaseous species and OC concentration show a good correlation, as is appreciate in Fig. 4b, and thus verifying their secondary source these aerosols.

### 3.2. Secondary organic aerosol determinations

Fig. 5 shows the OC and EC concentrations in $PM_{2.5}$ matter collected in early morning, from 6:00 to 10:00 h in February 2004, under low solar radiation intensity at Las Condes station. The slope and intercept of the linear regression, according to equation (1), represent the primary ratio ($[OC/EC]_p$) and the non-combustion primary OC contribution ($b$), respectively. In the same period, similar behaviour was observed in all stations. The slope $[OC/EC]_p$, $b$, and the linear regression coefficient ($r^2$) determined for all the stations are given in Table 2.

It is observed that in the three stations the slopes are almost identical thus suggesting that in the early morning period, the emission patterns of the sources present analogous characteristics. The different values of non-combustion primary OC parameter $b$, determines a different background ascribed to every place where different local meteorological conditions and different nocturnal activity can be found. Acceptable correlation values between OC

**Table 4**
Total Carbon (TC) in $PM_{2.5}$, Organic (OC) and Elemental Carbon (EC) fractions in percentage of the total carbon (TC) in the period of the February 2004 at the station under study.

| Stations[a] | TC[b] ($\mu g\,m^{-3}$) | OC (%) | EC (%) |
|---|---|---|---|
| Las Condes (M) | $7.9 \pm 3.1$ | 80 | 20 |
| Parque O'Higgins (N) | $6.2 \pm 4.4$ | 85 | 15 |
| Pudahuel (O) | $5.3 \pm 2.5$ | 86 | 14 |

[a] Labels are according to Fig. 1.
[b] Values represent diurnal average (10.00–18.00 h) $\pm$ standard deviation.

**Table 5**
Total organic aerosols (TOA), Primary Organic Aerosol (POA) and Secondary organic aerosols (SOA) fractions in the total organic aerosol according to EC tracer method in $PM_{2.5}$ in the period of the February 2004 at the station under study.

| Stations[a] | TOA[b] ($\mu g\,m^{-3}$) | POA (%) | SOA (%) |
|---|---|---|---|
| Las Condes (M) | $6.4 \pm 1.4$ | 80 | 20 |
| Parque O'Higgins (N) | $6.0 \pm 1.3$ | 91 | 9 |
| Pudahuel (O) | $5.3 \pm 0.6$ | 94 | 6 |

[a] Labels are according to Fig. 1.
[b] Values represent diurnal average (10.00–18.00 h) $\pm$ standard deviation.

and EC for $PM_{2.5}$ matter in all sites under study indicate that these results satisfy equation (1).

Based on these results, we applied the EC tracer method to the atmospheric conditions in Santiago City in order to determine the corresponding fractions of the primary and secondary organic carbon aerosols in our three monitoring stations of $PM_{2.5}$.

### 3.3. SOA based on daily determinations

In order to estimate the OC contribution to the secondary aerosol fraction, we have calculated the corresponding percentage of inorganic and organic fraction averages in the $PM_{2.5}$ masses collected during February 2004 in all stations under study. These values are presented in Table 3. In general, it is observed that the inorganic and organic fraction contributions to $PM_{2.5}$ are in the average 78% and 22% respectively.

From equation (2) and the linear regression constants shown in Table 2, it is possible to estimate the SOA and POA contributions to the organic fraction. This was done for a daytime period between 10.00 and 20.00 h and integrated on a daily basis from the organic fraction data obtained in February 2004. Thus, in Table 4 we present the OC and EC fractions in the organic fraction, OF, while in Table 5 the corresponding SOA and POA fractions are given.

These results shown in Table 5 are similar to other SOA fractions reported in other cities of USA and Europe (Russell and Allen, 2004; Plaza et al., 2006; Viana et al., 2007; Lonati et al., 2005; Chu et al., 2004; Fang et al., 2008). For example, in some areas of Texas, USA (Russell and Allen, 2004) and in Hong Kong city (Yu et al., 2004), some researchers have observed SOA concentrations from 0.6 to 1.2 $\mu g\,m^{-3}$, a similar range as the one determined from our data, 0.3 $\mu g\,m^{-3}$ to 1.3 $\mu g\,m^{-3}$, that representing between 6% and 20% of total organic aerosol matter (Table 5). Nevertheless, in Madrid,
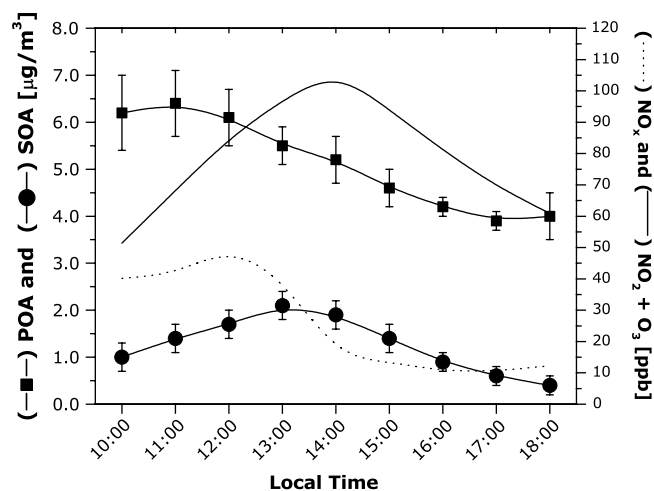


**Fig. 6.** Primary (POA) and secondary (SOA) organic aerosols in $PM_{2.5}$ and nitrogen oxides ($NO_x$) and Oxidants ($NO_2 + O_3$) concentration at Las Condes station (M label in Fig. 1) in February 2004.

Spain and Milan, Italy, show in summer time, values slightly higher than ours, 35% and 24%, respectively (Favez et al., 2007; Plaza et al., 2006; Lonati et al., 2005).

Finally, in Fig. 6 we show the hourly POA and SOA averages estimated for the time period from 10:00 h to 18:00 h in February 2004, at Las Condes station. SOA follows a classical pattern according to the photochemical evolution of the daily oxidative trends, where the maximum is attained close to the maximum of the solar radiation intensity. In the figure, we have incorporated the daily oxidant concentration average $(NO_2 + O_3)$ measured in the same period, allowing us to corroborate the origin of SOA as a secondary source. In turns, in the same period $NO_x$ concentration follows the POA concentration trend, thus verifying the origin of POA as a primary source.

## 4. Conclusions

We have measured the EC and OC concentrations in the $PM_{2.5}$ mass collected in the urban atmosphere of Santiago City during the period 2002–2005. Also, we have estimated the POA and SOA concentrations in $PM_{2.5}$ during February 2004. Some final remarks are:

(1) OC and EC concentrations measured in $PM_{2.5}$ particulates show a significant seasonal variation. EC concentrations registered in winter were higher than those obtained in summer at all sites under this study. A similar behavior was observed for OC concentrations. This seasonal variation can be attributed to the incremental emission by residential heating, and meteorological conditions.
(2) The carbonaceous species (OC and EC) represent a significant component in $PM_{2.5}$, which reaches from 19% to 26% in mass. However, OC is the dominant component, accounting at least 80% of the total carbon at the three sites under study.
(3) Our results according to the application of EC tracer method, show that the formation of SOA have an impact on $PM_{2.5}$ mass during summer time, February 2004, reaching up to 20% of total organic aerosol matter.

Since there is possible that some undetermined facts could modify the behavior of the emission intensities by different sources, thus affecting the $[EC/OC]_p$ ratio and the non-combustion contribution $(b)$, in future works it would be important to have periodical determination of the EC/OC ratio in order to estimate SOA and analyze the effect of the variations in $[EC/OC]_p$ over the estimation of SOA.

## Acknowledgements

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