

A study of the particulate matter PM₁₀ composition in the atmosphere of Chillán, Chile

José E. Celis^{a,*}, José R. Morales^b, Claudio A. Zaror^c, Juan C. Inzunza^d

^a *Facultad de Ingeniería Agrícola, Universidad de Concepción, Av. Vicente Mendez 595, Casilla 537, Chillán, Chile*

^b *Facultad de Ciencias, Universidad de Chile, Casilla 653, Santiago, Chile*

^c *Facultad de Ingeniería, Universidad de Concepción, Casilla 160-C, Concepción, Chile*

^d *Facultad de Ciencias Físicas y Matemáticas, Universidad de Concepción, Casilla 160-C, Concepción, Chile*

Received 7 January 2003; received in revised form 26 June 2003; accepted 30 June 2003

Abstract

Inhalable particulate matter (PM₁₀) concentrations were measured over 24-h intervals at six different urban sites in the city of Chillán from September 2001 to April 2003. Sampling locations were selected to represent central city, commercial, residential, and industrial portions of the city. Chemical composition of PM₁₀ was performed to samples of 47 mm diameter Teflon membranes within the city of Chillán. The spatial and temporal variability of the chemical composition of PM₁₀ was evaluated taking into account additional data from meteorology and further air pollutants. The majority of PM mass was comprised of carbon, nitrate, sulfate, ammonium, and crustal components but in different proportion on different days and at different sites. The chemical analyses showed that carbonaceous substances and crustal material were the most abundant component of PM₁₀ during the winter and summer, respectively. The concentrations of PM₁₀ were higher during the cold season than during the warm season. The PM₁₀ concentrations were higher in the downtown area of the city of Chillán, where also the chemical composition was more variable due to urban traffic and other anthropogenic sources.

© 2003 Elsevier Ltd. All rights reserved.

Keywords: Air contamination; Aerosols; Urban atmosphere; Particulate matter; Air pollution

1. Introduction

Several epidemiological studies have demonstrated a direct association between atmospheric inhalable particulate matter (PM₁₀) and respiratory diseases, pulmonary damage, and mortality among population (Dockery et al., 1993; Schwartz et al., 1996; Hoek et al., 1997; Harrison and Yin, 2000; Samet et al., 2000).

Aerosol particles are produced by natural and human activities. Typical natural sources are those that come from the sea and give origin to saline particles or wind-

blown dust. Man generates particulate matter as a result of industrial activities, traffic and combustion processes (Querol et al., 2001).

The chemical composition of particulate matter may vary according to the sources of the particles and the conditions of their dispersion (Eldred et al., 1997; Müller, 1999; Chow et al., 2002). A similarity in studies made in cities of industrialized countries has been observed, whereas in cities of the developing countries the variability is enormous due to large polluting loads and dust caused by local winds. In Chile, studies concerning particulate matter have been focused in the city of Santiago (Préndez and Carrasco, 1982; Préndez and Ortíz, 1982; UChile, 1999), and few investigations have been performed in cities along the territory with a population ranging between 50 000 and 250 000. Nevertheless, these

* Corresponding author. Tel.: +56-42-208-808; fax: +56-42-275-303.

E-mail address: jcelis@udec.cl (J.E. Celis).

cities are considered to be growing more quickly in Latin America, and those that present major expectations having a sustainable development (sustainable economic growth, social fairness and environmental protection). It is necessary to avoid that these cities reproduce the environmental problems of the metropolitan areas, so is important to evaluate quickly and strategically its environmental potentialities and limitations. The objective of this research was to analyse the chemical composition of the particulate matter PM_{10} in the city of Chillán, considering its temporary and space variability.

2. Methods

This study was carried out in the city of Chillán (Chile), which has a population of 162 930 people living in an urbanized surface of 2010 hectares. It is located in the northern central part of the Biobío region, between $36^{\circ}34'$ S latitude and 72° W longitude, and 144 m altitude above sea level. The surrounding lands are the result of fluvial and volcanic deposits, characterized by a flat topography with smooth slopes. These deposits were transported from the Andes Mountain by the rivers, as a result of huge volcanic and torrential events. Its climate is mediterranean with prolonged dry station (6 months) followed by a humid period, and 1100 mm annual average precipitation.

The study was performed between 1 September 2001 and 30 April 2003. The concentrations of particulate

matter PM_{10} were measured in six stationary points within the city of Chillán, by using IMPROVE monitors equipped with a Sierra Andersen 246b cyclone on 47 mm Teflon filters (Gelman Scientific, Ann Arbor, MI). The samplers were positioned taking into account traffic and stationary sources with significant contribution to the emissions (downtown, near to hospital, industries, and other sites), considering prevailing N–S wind direction (Fig. 1). The capture of particles was made with a flow rate of 16.7 l/min. Monitoring daily programming time was between 0:00 and 24:00 h for the monitor.

In each sampling site, the monitoring program allowed to collect particulate matter PM_{10} . The concentration ($\mu\text{g}/\text{m}^3$) of PM_{10} was determined by using a Cahn 31 microbalance, so filters were weighed before and after each 24-h sampling of continuous monitoring. For the determination of the chemical compounds in the filters, 25 elements (S, Cl, K, Ca, Ti, V, Cr, Mn, Fe, Ni, Cu, Zn, As, Pb, Se, Br, Rb, Sr, Zr, Mo, Na, Mg, Al, Si, P) were analysed by means of PIXE and energy-dispersive X-ray fluorescence spectrometry. A description of these techniques is in the literature available (Eldred et al., 1987; Brook et al., 1997). Filters were used to determine organic carbon (OC) by means of an optical analyser thermal DRI model 4000X. The concentration of organic matter (OM) was obtained multiplying the content of OC by a factor 1.4 (Eldred et al., 1997; Kim et al., 2000). EC was determined with a thermographic method, following the procedure detailed by Rööslä et al. (2001). The analysis to detect ammonium (NH_4^+) was made by

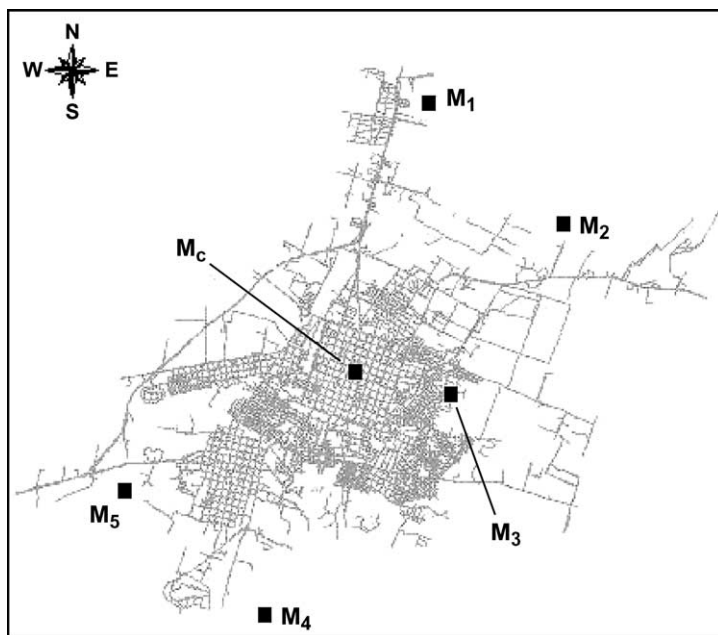


Fig. 1. Location of the monitors in the city of Chillán, Chile (where M_1, \dots, M_5 corresponds to monitoring stations in different sites within the city, with M_c located in the downtown area, of heaviest vehicular traffic in the city).

means of a spectrometer Lambda 2 Perkin Elmer. As suggested by Chow and Watson (1999), the ions nitrate (NO_3^-), sulfate (SO_4^{2-}) and chloride (Cl^-) were determined by ion chromatography (Dionex DX 100).

In order to calculate the proportion of soil (wind-blown dust) in PM_{10} , the equation proposed by Aldape et al. (1991) was used here: $\text{Soil} = 2.20\text{Al} + 2.49\text{Si} + 1.63\text{Ca} + 1.94\text{Ti} + 2.38\text{Fe}$, where Si, Al, Fe, Ca, and Ti are the concentrations of those elements in $\mu\text{g}/\text{m}^3$.

Potassium is in natural form in the ground, but also it is present in the smoke of the combustion from vegetative biomass, so producing soluble K. In Chillán, wood

is a common fuel for housing heating, so producing visually dense smoke clouds in cold months. In order to calculate the amount of non-geologic potassium, the equation suggested by Eldred et al. (1987) was used: $K_{\text{nos}} = K - 0.6\text{Fe}$, where K and Fe are the concentrations of those elements ($\mu\text{g}/\text{m}^3$).

Each monitor was equipped to handle four cassettes plus an internal programmable clock, which allowed changing filters and equipment maintenance every five days. Approximately 1800 filters were collected throughout the study, which were used to determine the mass of the PM_{10} . Monthly, in each site of monitoring it

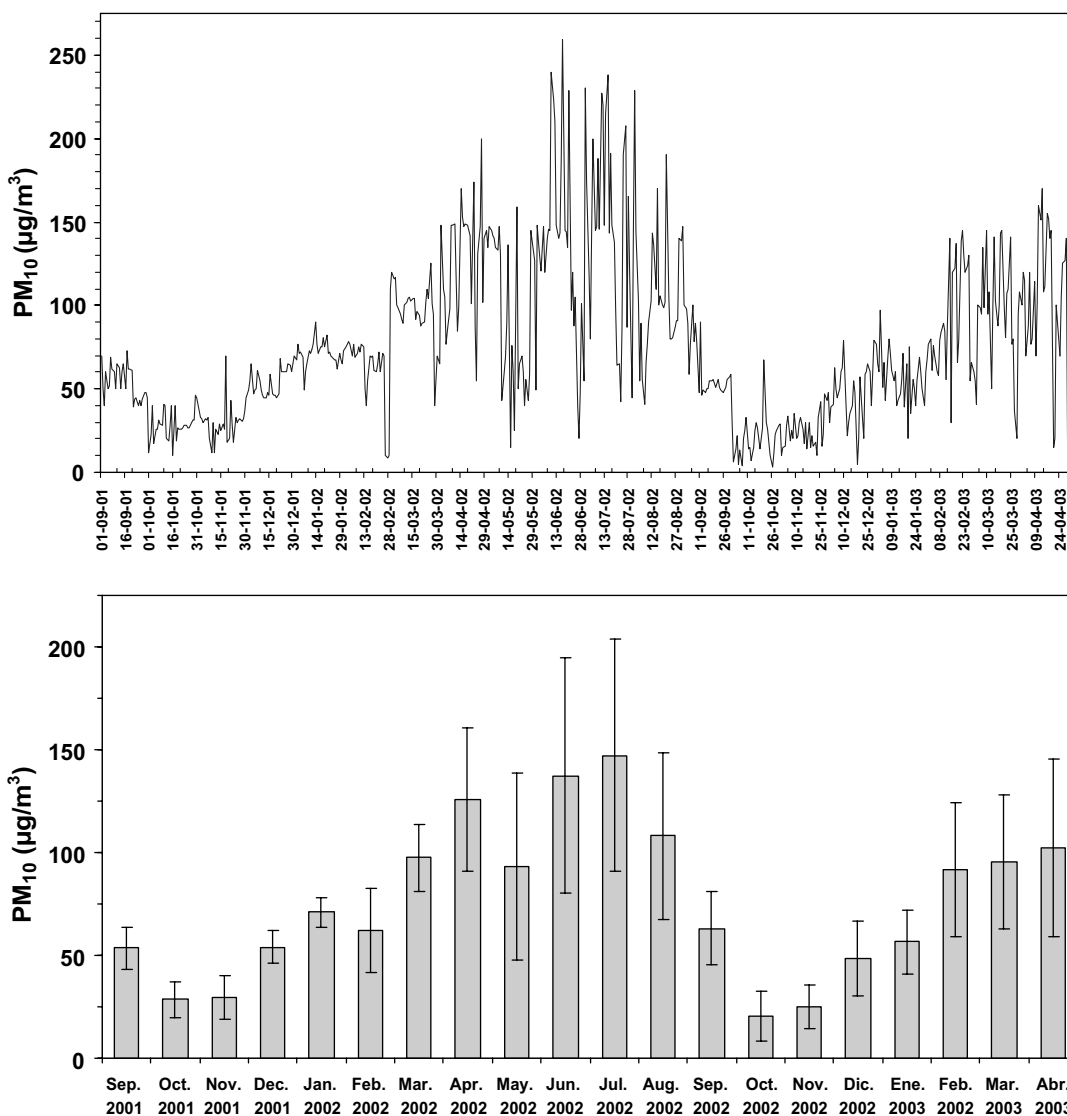


Fig. 2. Temporal variations of PM_{10} mass concentrations within the urban environment of Chillán between 1 September 2001 and 30 April 2003.

was prepared a mixed sample for the chemical analyses: 10 filters for analysis of ions, three filters to determine carbon, and 10 filters for determination of elemental concentration. For the mixed samples the selected filters were shredded to small pieces of about 1 cm², macerated with nitric acid (65%) and centrifuged. The weather data (temperature, wind speed and relative humidity) were obtained from the meteorological station at the University of Concepcion, located in the limit of the city of Chillán. Also, these variables were measured at downtown during the present research by means of a datalogger Campbell Scientific 21 XL.

3. Results and discussion

In Fig. 2 is showed the average daily and monthly inhalable particulate matter concentration during the entire period of the study. Each value is the result of the average of six monitoring stations located as shown (Fig. 1). PM₁₀ was clearly higher during the cold season (March–August) than during the warm months

(September–February). The annual average PM₁₀ concentration measured from 1 September 2001 to 30 September 2002 of 82.5 ± 48.7 µg/m³ exceeded the US air quality standard (50 µg/m³) and the European limit (40 µg/m³). The annual average measured from 1 January to 31 December 2002 of 83.4 ± 51.6 µg/m³ also exceeded the air quality standards. Twenty four days exceeded the 24-h US air quality standard of 150 µg/m³. Maximum PM₁₀ concentrations were found on 10 and 17 June 2002 with 259.1 ± 51.7 and 239.8 ± 45.6 µg/m³, respectively.

In Table 1 is showed the seasonal and average chemical composition of PM₁₀ in Chillán during 2001 and 2002: Spring (21 September–21 December), Summer (22 December–21 March), Autumn (22 March–21 June), and Winter (22 June–21 September). Each seasonal value is the result of the average of six stations with continuous monitoring. As shown in Fig. 3, the main constituent of PM₁₀ at Chillán sites was found to be organic matter (31%), followed by soil (27%), nitrate (11%), elemental carbon (8%), ammonium (7%), sulfate (5%), and non-geologic potassium (1%), whereas most prominent elements were Si, K, Fe, Ca, Al, Cl, Zn, Ti,

Table 1
Chemical composition of PM₁₀ (µg/m³) in the urban atmosphere of Chillán between September 2001 and April 2003

| | Spring | Summer | Autumn | Winter | Mean value | Maximum |
|-----------------|--------------|---------------|---------------|---------------|---------------|--------------------|
| OM | 12.91 ± 9.79 | 17.15 ± 11.75 | 39.67 ± 19.29 | 34.42 ± 25.02 | 23.12 ± 18.56 | 84.98 ^a |
| NO ₃ | 4.73 ± 2.42 | 6.42 ± 2.95 | 17.29 ± 6.83 | 11.32 ± 8.33 | 8.60 ± 6.33 | 27.88 |
| EC | 5.40 ± 2.45 | 5.84 ± 2.09 | 6.63 ± 2.80 | 5.87 ± 2.89 | 5.95 ± 2.61 | 12.01 ^a |
| NH ₄ | 3.65 ± 1.26 | 3.11 ± 1.36 | 6.35 ± 1.62 | 7.96 ± 2.84 | 4.78 ± 2.74 | 14.50 |
| SO ₄ | 2.05 ± 0.65 | 1.76 ± 1.12 | 6.12 ± 2.12 | 6.67 ± 2.77 | 4.15 ± 1.47 | 13.42 ^b |
| Si | 3.02 ± 1.26 | 9.19 ± 2.34 | 1.34 ± 3.47 | 1.01 ± 2.04 | 3.64 ± 7.38 | 14.50 |
| Fe | 2.45 ± 0.21 | 4.75 ± 0.53 | 0.95 ± 0.12 | 0.29 ± 0.10 | 2.11 ± 0.36 | 6.27 |
| Al | 1.87 ± 0.05 | 3.28 ± 0.51 | 0.36 ± 0.04 | 0.18 ± 0.16 | 1.42 ± 0.16 | 4.31 |
| Ca | 2.14 ± 0.24 | 3.65 ± 0.24 | 0.42 ± 0.13 | 0.23 ± 0.05 | 1.61 ± 0.21 | 4.90 |
| Sr | 0.05 ± 0.28 | 0.07 ± 0.15 | 0.01 ± 0.14 | 0.00 ± 0.21 | 0.03 ± 0.18 | 0.32 |
| As | 0.00 ± 0.05 | 0.00 ± 0.04 | 0.00 ± 0.06 | 0.07 ± 0.15 | 0.02 ± 0.05 | 0.105 |
| K | 0.98 ± 0.23 | 0.51 ± 0.35 | 4.21 ± 0.87 | 1.98 ± 0.03 | 1.91 ± 0.65 | 5.61 ^a |
| Ti | 0.11 ± 0.04 | 0.17 ± 0.13 | 0.03 ± 0.65 | 0.70 ± 0.48 | 0.25 ± 0.26 | 0.91 ^a |
| Cl | 0.34 ± 0.05 | 0.30 ± 0.04 | 0.41 ± 0.23 | 0.23 ± 0.23 | 0.32 ± 0.12 | 0.654 |
| Zn | 0.08 ± 0.02 | 0.23 ± 0.11 | 0.38 ± 0.14 | 0.51 ± 0.19 | 0.30 ± 0.12 | 0.61 |
| Pb | 0.01 ± 0.04 | 0.01 ± 0.12 | 0.03 ± 0.11 | 0.03 ± 0.21 | 0.02 ± 0.11 | 0.262 ^a |
| Cu | 0.22 ± 0.02 | 0.24 ± 0.05 | 0.15 ± 0.10 | 0.11 ± 0.15 | 0.18 ± 0.05 | 0.31 |
| Mn | 0.02 ± 0.15 | 0.03 ± 0.12 | 0.04 ± 0.16 | 0.08 ± 0.04 | 0.04 ± 0.15 | 0.247 ^a |
| Se | 0.00 ± 0.03 | 0.02 ± 0.26 | 0.01 ± 0.35 | 0.01 ± 0.18 | 0.01 ± 0.23 | 0.05 ^b |
| Ni | 0.01 ± 0.05 | 0.02 ± 0.06 | 0.01 ± 0.09 | 0.01 ± 0.10 | 0.01 ± 0.08 | 0.035 ^a |
| V | 0.01 ± 0.03 | 0.01 ± 0.05 | 0.03 ± 0.04 | 0.00 ± 0.26 | 0.02 ± 0.05 | 0.075 ^a |
| Ba | 0.11 ± 0.02 | 0.13 ± 0.04 | 0.14 ± 0.05 | 0.15 ± 0.06 | 0.13 ± 0.04 | 0.223 |
| S | 0.02 ± 0.04 | 0.01 ± 0.05 | 0.05 ± 0.06 | 0.10 ± 0.03 | 0.05 ± 0.05 | 0.291 ^b |
| Mg | 0.37 ± 0.05 | 0.41 ± 0.06 | 0.26 ± 0.08 | 0.12 ± 0.05 | 0.29 ± 0.06 | 0.532 |
| Mo | 0.01 ± 0.03 | 0.02 ± 0.01 | 0.07 ± 0.05 | 0.08 ± 0.03 | 0.05 ± 0.02 | 0.101 ^a |
| Br | ND | 0.005 ± 0.003 | 0.021 ± 0.012 | 0.004 ± 0.002 | 0.01 ± 0.02 | 0.07 ^a |

The maximum value indicates the highest concentration registered in the period.

ND = Not Detectable.

^a Values corresponding at downtown area (M_c).

^b Value corresponding to hospital location (M₃).

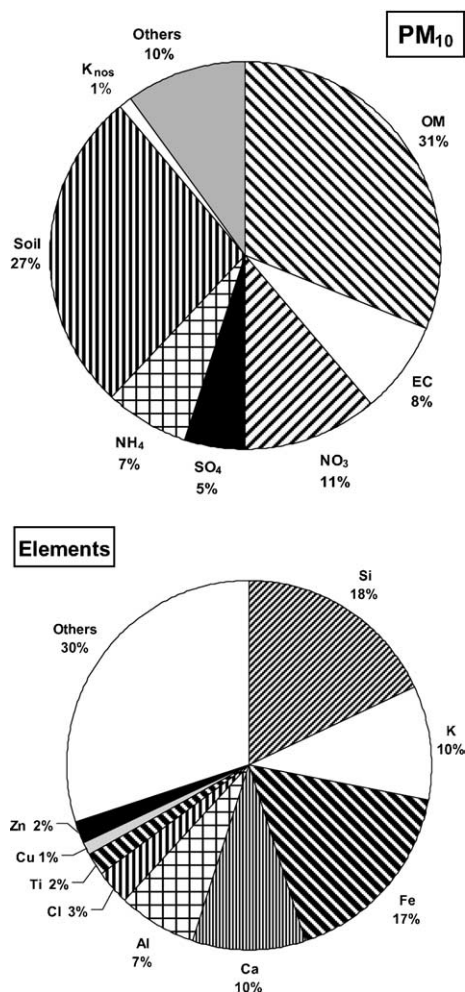


Fig. 3. Relative percentage of chemical composition of PM₁₀ within the city of Chillán between September 2001 and April 2003.

and Cu. The components OM, EC, and NO₃ result from combustion gases of vehicles and firewood burning (Turnbull and Harrison, 2000; Gillies et al., 2001), whereas the ammonium is originated from agricultural activities as well as from vehicles with catalysts and industrial sources (Harrison and Yin, 2000). Particularly, OM is of primary as well as secondary origin (Röösli et al., 2001). The nitrate concentration is directly associated with the traffic of the city because it is formed from the NO₂. The Cl comes from the ocean and is an element that normally is present in soluble form in nature, so is generally part of the atmosphere of most Chilean cities (Hrepić et al., 1983).

Higher NO₃, OM, EC, NH₄, V, Zn, K, Mo, Mn, Cl, and Ni concentrations were found in cold season than in warm months. On the other hand, higher concentrations of Si, Al, Ti, Ca, Sb, and Fe were registered

during summertime (December–March) than during cold months. This finding are similar to results registered in recent studies abroad (Müller, 1999; Turnbull and Harrison, 2000; Gillies et al., 2001; Röösli et al., 2001), suggesting that air pollution during the cold season originates from anthropogenic sources, whereas in summertime comes from natural sources. The high concentration of Si, Al, Fe, and Ca during summertime can be explained by re-suspension of dust from roads and surrounding agricultural lands. Originally, soils of the Chilean Central Valley were mostly formed from volcanic ashes, therefore easily release many particles by action of the wind and farming activities, specially when they are dried. In addition with that, 60% of the urban streets in the city of Chillán still remain unpaved (Celis et al., 2003).

A seasonal pattern was observed for lead. There was an increase in May, June and July as compared to December, January and February. It is necessary to emphasize that leaded gasoline was allowed in Chile until 1 March 2001. For that reason, present lead levels were lower than the levels found in a preliminary study performed in 1998 in the city of Chillán (Celis et al., 2002), and are similar to the city of Santiago, where lead is also decreasing following the same tendency (SESMA, 2002). In Europe, leaded gasoline was permitted until 1 January 2000 (Röösli et al., 2001). Copper is an abundantly natural element in Chilean soils, therefore its behaviour can strongly be related to the fraction of PM₁₀ originated by wind-blown dust. With regard to manganese, human population may be exposed to manganese released into the air by the combustion of the unleaded gas that contains the organic manganese compound, methylcyclopentadienyl-tricarbonyl-manganese as anti-detonant (SESMA, 2002).

The SO₄ concentration in the atmosphere of Chillán does not appear a crucial factor, in coincidence with data reported by Paoletti et al. (2002). The highest sulfate concentration corresponded to the monitoring station located near the local hospital (M₃), which has an energy plant with coal-fired boiler. High concentrations of non-crustal V and Ni (products of oil combustion emissions), Br, Pb, and NO₃ (products of the vehicle combustion), EC (product of diesel engines), OM and K (component from vehicle combustion and firewood burning) were measured at monitoring station M_c, located at downtown area. In the city of Chillán usually circulate public cars, buses and trucks that have been retired from circulation in the metropolitan region (Santiago), so for that reason they are the main responsible for these compounds.

In Table 2 monthly averages PM₁₀ concentrations are related to temperature, wind speed, relative humidity, and precipitation. In general, a higher concentration of PM₁₀ along with lower temperature, wind speed, precipitation, and increasing relative humidity was noted. A

Table 2

Monthly average concentration of PM₁₀ and meteorological parameters (September 2001 to April 2003) of Chillán, Chile

| | PM ₁₀ (µg/m ³) | Temperature (°C) | | Wind speed (m/s) | | Relative humidity (%) | | Precipitation (mm) |
|----------|---------------------------------------|------------------|----------------|------------------|----------------|-----------------------|----------------|--------------------|
| | | M ₂ | M _c | M ₂ | M _c | M ₂ | M _c | |
| Sep 2001 | 61.5 ± 3.9 | 10.1 ± 4.7 | 12.6 ± 3.2 | 2.0 ± 4.8 | 1.1 ± 2.6 | 77.1 ± 12.9 | 78.6 ± 11.5 | 29.8 |
| Oct 2001 | 38.3 ± 3.7 | 13.6 ± 1.8 | 16.5 ± 3.4 | 1.8 ± 2.8 | 0.8 ± 1.3 | 60.9 ± 8.9 | 79.4 ± 5.5 | 30.4 |
| Nov 2001 | 37.4 ± 2.9 | 15.0 ± 2.3 | 18.2 ± 5.3 | 2.2 ± 2.7 | 0.8 ± 1.4 | 67.7 ± 7.7 | 69.5 ± 6.8 | 34.8 |
| Dec 2001 | 73.5 ± 4.8 | 20.9 ± 2.6 | 23.5 ± 4.7 | 2.8 ± 3.4 | 1.3 ± 1.4 | 53.8 ± 6.5 | 57.3 ± 7.9 | 0.0 |
| Jan 2002 | 82.3 ± 5.9 | 20.3 ± 2.9 | 24.5 ± 4.3 | 2.1 ± 3.4 | 0.6 ± 1.0 | 55.7 ± 9.1 | 56.4 ± 9.7 | 0.0 |
| Feb 2002 | 78.5 ± 8.8 | 19.3 ± 5.1 | 22.8 ± 5.4 | 1.8 ± 2.3 | 0.5 ± 1.1 | 58.2 ± 13.8 | 60.2 ± 10.5 | 172.5 |
| Mar 2002 | 103.2 ± 10.8 | 15.2 ± 1.4 | 17.3 ± 4.8 | 1.6 ± 3.0 | 0.3 ± 1.6 | 74.9 ± 8.4 | 76.5 ± 8.8 | 55.8 |
| Apr 2002 | 127.4 ± 15.6 | 11.6 ± 2.2 | 14.5 ± 5.1 | 1.5 ± 3.7 | 0.4 ± 1.5 | 82.6 ± 6.2 | 84.4 ± 6.7 | 54.1 |
| May 2002 | 90.5 ± 18.7 | 9.1 ± 2.9 | 12.4 ± 4.9 | 1.8 ± 5.9 | 0.7 ± 1.2 | 90.2 ± 4.7 | 93.1 ± 5.5 | 283.0 |
| Jun 2002 | 130.2 ± 16.9 | 5.7 ± 3.3 | 9.2 ± 3.4 | 2.3 ± 5.0 | 0.8 ± 1.1 | 89.0 ± 5.9 | 93.6 ± 6.1 | 188.5 |
| Jul 2002 | 137.5 ± 14.4 | 6.8 ± 3.0 | 8.5 ± 2.7 | 2.1 ± 4.8 | 0.9 ± 1.7 | 89.6 ± 4.6 | 92.5 ± 4.4 | 160.4 |
| Aug 2002 | 105.2 ± 19.7 | 9.7 ± 2.2 | 11.8 ± 4.2 | 2.6 ± 6.1 | 1.2 ± 1.9 | 85.8 ± 6.2 | 87.3 ± 5.8 | 218.4 |
| Sep 2002 | 72.4 ± 9.5 | 10.2 ± 1.7 | 13.4 ± 3.3 | 1.8 ± 4.3 | 0.9 ± 1.3 | 78.9 ± 5.7 | 83.7 ± 6.3 | 86.5 |
| Oct 2002 | 27.4 ± 8.2 | 12.2 ± 1.7 | 15.8 ± 2.9 | 2.3 ± 1.1 | 1.9 ± 1.0 | 78.8 ± 8.6 | 79.1 ± 5.6 | 216.9 |
| Nov 2002 | 35.6 ± 10.8 | 14.2 ± 2.0 | 16.9 ± 2.5 | 2.2 ± 0.9 | 1.6 ± 1.2 | 74.6 ± 7.9 | 76.5 ± 3.5 | 59.5 |
| Dec 2002 | 64.1 ± 10.5 | 17.3 ± 1.8 | 19.8 ± 2.4 | 1.9 ± 0.5 | 1.1 ± 1.1 | 67.2 ± 5.5 | 70.3 ± 3.7 | 8.8 |
| Jan 2003 | 71.2 ± 11.9 | 19.9 ± 2.4 | 23.7 ± 2.1 | 2.8 ± 3.3 | 1.8 ± 1.9 | 59.1 ± 8.3 | 65.1 ± 3.3 | 11.7 |
| Feb 2003 | 121.1 ± 14.4 | 18.4 ± 2.1 | 21.6 ± 2.2 | 2.3 ± 4.6 | 1.2 ± 1.8 | 55.9 ± 7.5 | 61.3 ± 4.2 | 0.0 |
| Mar 2003 | 129.4 ± 20.3 | 17.6 ± 2.1 | 19.9 ± 2.6 | 1.7 ± 2.8 | 0.6 ± 1.3 | 66.3 ± 10.4 | 70.5 ± 3.8 | 8.5 |
| Apr 2003 | 137.5 ± 33.8 | 12.2 ± 3.5 | 14.9 ± 2.7 | 1.3 ± 3.5 | 0.5 ± 1.1 | 75.0 ± 16.1 | 79.5 ± 3.5 | 36.2 |
| Average | 86.2 ± 38.7 | 13.9 ± 5.5 | 16.9 ± 5.7 | 2.1 ± 4.6 | 1.0 ± 1.7 | 72.1 ± 3.9 | 75.8 ± 5.1 | |

Data is the mean value of the parameter between monitoring stations M_c and M₂ in the entire period of study.

similar correlation has been observed by Aldape et al. (1991), Rööslí et al. (2001), and Celis et al. (2003). Temperatures were lower during autumn and winter-time, so probably most of the particles become condensed instead of volatilising. Temperatures measured at downtown area were in average 21.6% higher than sites at urban limit, whereas wind speed was approximately 52% lower and relative humidity was 5% higher, suggesting a strong influence of human activity in the inhalable particulate matter.

As previously noted by Aldape et al. (1991), high correlations were found for the elements Pb, S, V, Mn and for Fe, Si, Al, Ca, Ti (Table 3). In the first case, a clear anthropogenic origin was observed, whereas the second group is a result of geologic sources. It is important to notice that there was a low correlation for K, as compared to Si and Fe, which suggests the presence of smoke in the atmosphere of Chillán, as a result of wood combustion from residential houses and municipal waste incinerators. Fig. 4 indicates that inhalable particulate matter is dominated with mineral particles to which occasionally smaller particles are attached; also aggregates of soot are present in this sample.

A clear temporary variability for OM, NO₃, NH₄, soil and K_{nos} was observed (Fig. 5). A seasonal pattern for EC was not observed. These results were similar to those of Rööslí et al. (2001). The values of OM, NO₃,

NH₄, and K_{nos} were higher during the cold months. On the other hand, the highest soil concentrations (Si, Al, Ca, K, Fe, and Ti) were measured in warm months. The fraction of potassium contained in products of the combustion from housing heating (K_{nos}) was prominent in cold months (between April and July), when wood is used massively in the city of Chillán, producing a dense smoke cloud that remains to very low height and that does not dissipate in those days with atmospheric stability (low temperature and wind speed, with high relative humidity).

In Fig. 6, a spatial and temporal variability of the chemical compounds at each monitoring sites in the city of Chillán is showed. The EC, OM, NH₄, and NO₃ concentrations were higher at downtown area (M_c). No seasonal pattern was clearly observed for EC, as previously noted by Rööslí et al. (2001). Ammonium concentrations were slightly greater at the limits of the city (monitoring station M₂) during September 2002, which is time coinciding with applications of pesticides and fertilizers on agricultural lands that surround the city of Chillán.

It is possible to note (Fig. 7) that higher soil concentration was clearly manifested between December and March (maximum in January), at those sites far apart of downtown (monitoring stations M₁ and M₂). The reason for that is because these points were at the

Table 3
Pearson correlation for the elements measured in the city of Chillán (September 2001 to April 2003)

| | Si | K | Fe | Ca | Al | Cl | S | Ti | Cu | Zn | Mn | Mg | Se | Pb | Sr | V |
|----|--------|--------|--------|-------|--------|-------|-------|--------|--------|--------|-------|-------|-------|-------|--------|-------|
| K | 0.435 | | | | | | | | | | | | | | | |
| Fe | 0.971 | 0.443 | | | | | | | | | | | | | | |
| Ca | 0.775 | 0.756 | 0.876 | | | | | | | | | | | | | |
| Al | 0.884 | 0.834 | 0.785 | 0.875 | | | | | | | | | | | | |
| Cl | 0.521 | 0.123 | -0.113 | 0.547 | 0.453 | | | | | | | | | | | |
| S | 0.224 | 0.456 | 0.552 | 0.432 | 0.279 | 0.689 | | | | | | | | | | |
| Ti | 0.855 | 0.884 | 0.874 | 0.769 | 0.904 | 0.435 | 0.653 | | | | | | | | | |
| Cu | 0.446 | 0.543 | 0.664 | 0.624 | 0.498 | 0.337 | 0.431 | 0.554 | | | | | | | | |
| Zn | -0.043 | -0.065 | 0.078 | 0.247 | -0.025 | 0.143 | 0.299 | -0.087 | 0.272 | | | | | | | |
| Mn | 0.583 | 0.674 | 0.679 | 0.453 | 0.407 | 0.231 | 0.773 | 0.154 | 0.155 | -0.017 | | | | | | |
| Mg | 0.152 | 0.123 | 0.134 | 0.332 | 0.345 | 0.189 | 0.284 | 0.256 | 0.169 | 0.032 | 0.378 | | | | | |
| Se | -0.093 | -0.065 | -0.012 | 0.178 | 0.127 | 0.036 | 0.517 | 0.112 | 0.235 | 0.432 | 0.231 | 0.432 | | | | |
| Pb | 0.437 | 0.354 | 0.231 | 0.358 | 0.236 | 0.054 | 0.805 | 0.357 | 0.201 | 0.321 | 0.755 | 0.213 | 0.189 | | | |
| Sr | 0.143 | 0.076 | 0.137 | 0.096 | 0.165 | 0.045 | 0.039 | 0.144 | -0.075 | -0.132 | 0.043 | 0.124 | 0.342 | 0.231 | | |
| V | 0.731 | 0.705 | 0.765 | 0.743 | 0.725 | 0.453 | 0.765 | 0.805 | 0.432 | 0.107 | 0.764 | 0.321 | 0.412 | 0.756 | -0.096 | |
| Ni | -0.145 | -0.034 | 0.324 | 0.234 | 0.357 | 0.234 | 0.323 | 0.136 | 0.045 | 0.238 | 0.436 | 0.125 | 0.123 | 0.234 | 0.124 | 0.154 |

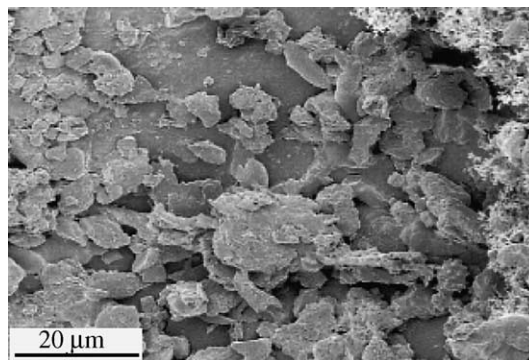


Fig. 4. Electronic microscopy of a PM₁₀ sample collected in the city of Chillán, Chile (June 5, 2002).

edge of the city of Chillán, so received direct emissions from lands that surround the urban area, and also for re-suspension of dust from roads produced by urban and rural traffic and that is transported by prevailing wind direction (during spring and summertime was from southwest). It is necessary to note that Chillán still has a 60% of streets without paving. Non-geologic potassium levels (K_{nos}) from the combustion of wood were present during the cold season (April–July), being the highest at downtown.

4. Conclusions

The results obtained in this research showed that there was a distribution pattern of the chemical components in the inhalable particular matter as a function of the anthropogenic activity within the city of Chillán. The chemical analyses of PM₁₀ revealed that carbonaceous substances (EC, OM), crustal material and inorganic substances of secondary origin (NO₃ and NH₄) are the predominant components of PM₁₀ in the city of Chillán during September 2001 to April 2003 (approximately 90%). A clear temporal variability was observed, because there was a higher concentration of PM₁₀ during cold season than during the warm months. Also, spatial variability was noted as downtown of Chillán resulted more contaminated by chemical compounds (OM, NO₃, NH₄, EC, K_{nos}, Ti, K, Pb, Mn, Ni, V, and Mo) compared to surrounding areas of the city. Perimetrical areas receive large loads of geologic material in suspension in summertime. In general, there were no high SO₄ concentrations in the city of Chillán, which can be explained for there are few industries nearby. However, it is a matter of a worry the highest levels of this compound are at the hospital location, with large combustion installations burning fuel coal the year throughout.

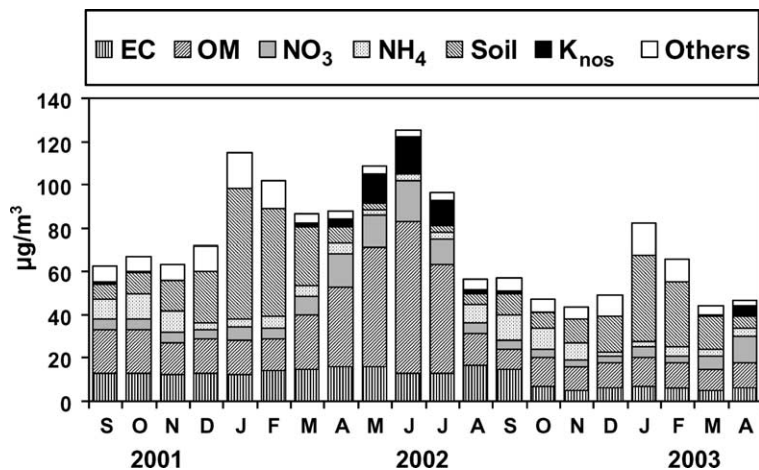


Fig. 5. Monthly average variation of the chemical components of PM_{10} within the city of Chillán for the period September 2001 to April 2003.

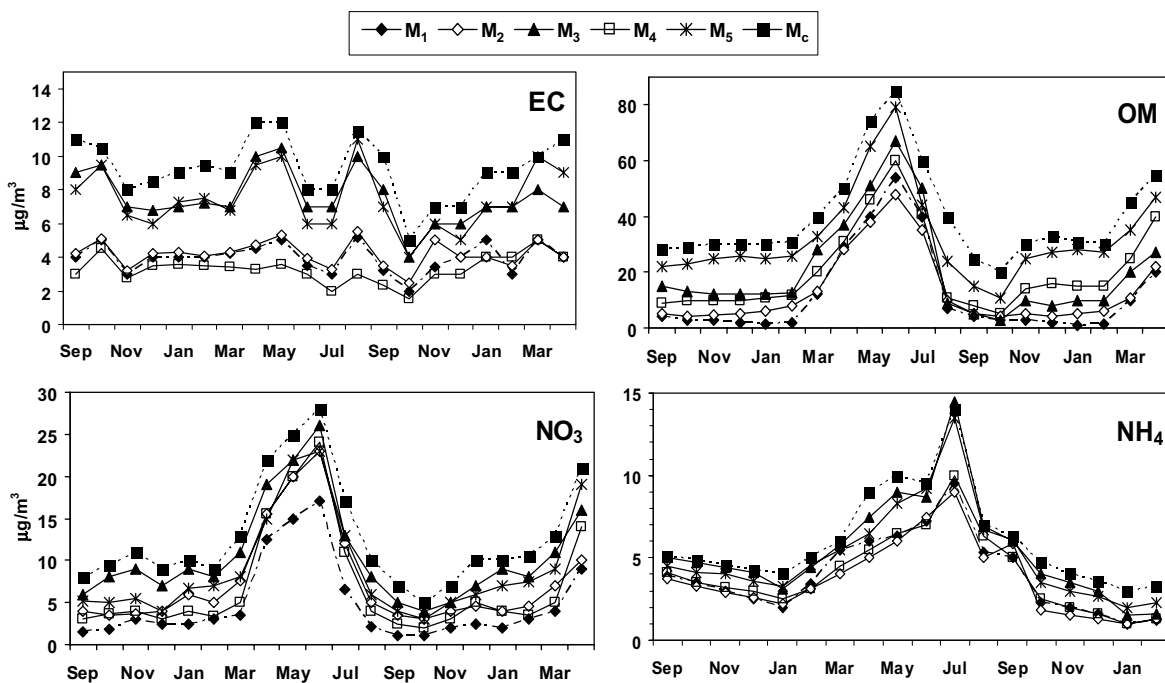


Fig. 6. Temporal and spatial variation of the chemical composition of PM_{10} in the city of Chillán between September 2001 and April 2003.

The results, even though from limited coverage, indicate that the inhalable atmosphere of the city of Chillán is to be considered as a problem of anthropogenic origin during autumn and winter. This was explained mainly due to the massive use of wood as fuel for residential heating and urban traffic within

urban areas of the city, so producing a dense smoke cloud in those days of atmospheric stability. It is recommended to accomplish a cadastre of emissions for the city of Chillán, thus to identify the contributions from stationary point sources and traffic pollutants.

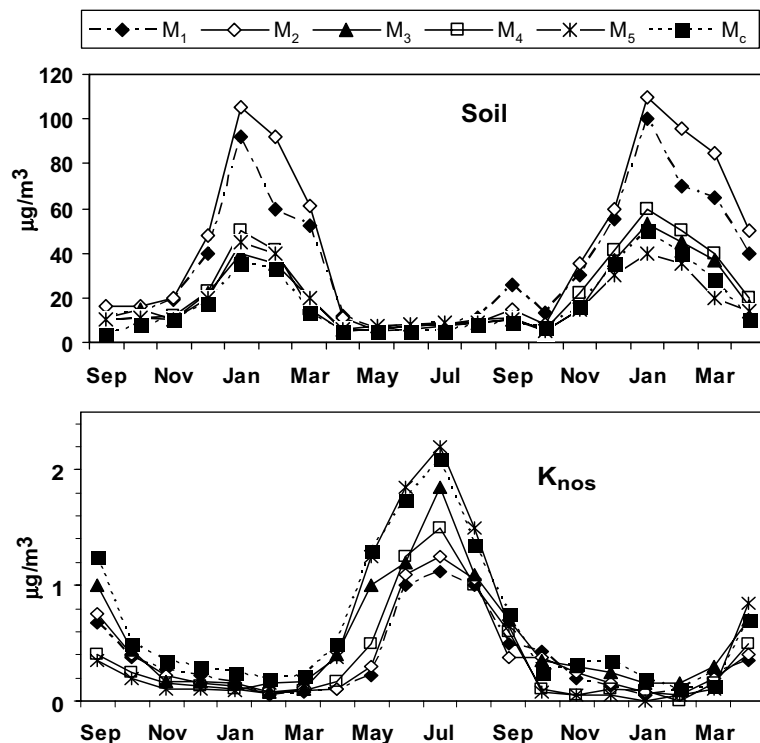


Fig. 7. Inhalable particulate matter concentration in the soil fraction and wood combustion of Chillán (September 2001 to April 2003).

Acknowledgements

This study was partly supported by projects P.I. 200.132.004-1.1 and Instrumentación Científica “Sistema de Medición de Variables Ambientales”, both from the Dirección de Investigación de la Universidad de Concepción. Also, many thanks to the Crocker Nuclear Laboratory of the University of California (Davis), for providing the IMPROVE PM₁₀ monitors and allowing most of the chemical analyses. This work was part of the corresponding author’s Ph.D thesis in Environmental Sciences at the Centro EULA of the Universidad de Concepción, Chile.

References

- Aldape, F., Flores, J., Díaz, R., Miranda, J., Cahill, T., Morales, J., 1991. Two year study of elemental composition of atmospheric aerosols in México City. I. J. PIXE 1, 373–388.
- Brook, J.R., Dann, T.F., Burnett, R.T., 1997. The relationship among TSP, PM₁₀, PM_{2.5} and inorganic constituents of atmospheric particulate matter at multiple Canadian locations. J. Air Waste Manage. Assoc. 47, 2–19.
- Celis, J., Carvacho, O., Flocchini, R., Cañumir, J., Flores, A., 2002. Monitoreo preliminar del material particulado en suspensión en las afueras de la ciudad de Chillán. Agro-Ciencia 18, 133–142.
- Celis, J., Morales, R., Zaror, C., Inzunza, J., Flocchini, R., Carvacho, O., 2003. Chemical characterization of the inhalable particulate matter in the city of Chillán, Chile. J. Chil. Chem. Soc. 48 (2), 47–53.
- Chow, J., Watson, J., Edgerton, S., Vega, E., 2002. Chemical composition of PM_{2.5} and PM₁₀ in Mexico City during winter 1997. Sci. Total Environ. 287, 177–201.
- Chow, J., Watson, J., 1999. Ion chromatography. In: Landsberger, S., Creatchman, M. (Eds.), Elemental Analysis of Airborne Particles. Gordon and Breach, Newark, NJ, pp. 97–137.
- Dockery, D., Pope, C., Xu, X., Spengler, J., Ware, J., Fay, M., Ferris, B., Speizer, F., 1993. An association between air pollution and mortality in six US cities. N. Engl. J. Med. 329, 1753–1759.
- Eldred, R., Cahill, T., Feeney, P., 1987. Particulate monitoring at US national parks using PIXE. Nucl. Instr. and Meth. B 22, 289–295.
- Eldred, R., Cahill, T., Flocchini, R., 1997. Composition of PM_{2.5} and PM₁₀ aerosols in the IMPROVE network. J. Air Waste Manage. Assoc. 47, 194–203.
- Gillies, J., Gertler, A., Sagebiel, J., Dippel, W., 2001. On-road particulate matter (PM_{2.5} and PM₁₀) emissions in the Sepulveda tunnel, Los Angeles, California. Environ. Sci. Technol. 35, 1054–1063.
- Harrison, R., Yin, J., 2000. Particulate matter in the atmosphere: which particle properties are important for its effect on health? Sci. Total Environ. 249, 85–101.

- Hoek, G., Schwartz, J., Groot, B., Eilers, P., 1997. Effects of ambient particulate matter and ozone on daily mortality in Rotterdam, The Netherlands. *Arch. Environ. Health* 52, 455–463.
- Hrepic, N., Mladinic, P., Díaz, C., Préndez, M., 1983. Estudio preliminar de la contaminación atmosférica por material particulado en la ciudad de Arica. *Bol. Soc. Chil. Quím.* 28, 477–479.
- Kim, B., Teffera, S., Zeldin, M., 2000. Characterization of PM_{2.5} and PM₁₀ in the south coast air basin of southern California: Part 1—Spatial variations. *J. Air Waste Manage. Assoc.* 50, 2034–2044.
- Müller, K., 1999. A three year study of aerosol in north-west Saxony (Germany). *Atmos. Environ.* 33, 1679–1685.
- Paoletti, L., De Berardis, B., Diociaiuti, M., 2002. Physico-chemical characterisation of the inhalable particulate matter (PM₁₀) in an urban area: an analysis of the seasonal trend. *Sci. Total Environ.* 292, 265–275.
- Préndez, M., Ortíz, J., 1982. Estudio de la contaminación atmosférica por material particulado en la ciudad de Santiago. *Bol. Soc. Chil. Quím.* 27, 283–285.
- Préndez, M., Carrasco, M., 1982. Influencia del tráfico vehicular en la contaminación atmosférica por material particulado en la ciudad de Santiago. *Bol. Soc. Chil. Quím.* 27, 310–312.
- Querol, X., Alastuey, A., Rodríguez, S., Plana, F., Mantilla, E., Ruiz, C., 2001. Monitoring of PM₁₀ and PM_{2.5} around primary particulate anthropogenic emission sources. *Atmos. Environ.* 35, 845–858.
- Röösli, M., Theis, G., Künzli, N., Staehelin, J., Mathys, P., Oglesby, L., Camenzind, M., Braun-Fahrländer, Ch., 2001. Temporal and spatial variation of the chemical composition of PM₁₀ at urban and rural sites in the Basel area, Switzerland. *Atmos. Environ.* 35, 3701–3713.
- Samet, J., Dominici, F., Curriero, F., Coursac, I., Zeger, S., 2000. Fine particulate air pollution and mortality in 20 US cities, 1987–1994. *N. Engl. J. Med.* 343, 1742–1749.
- Schwartz, J., Dockery, D., Neas, L., 1996. Is daily mortality associated specifically with fine particles? *J. Air Waste Manage. Assoc.* 46, 2–14.
- SESMA (Servicio de Salud Metropolitano del Ambiente), 2002. Caracterización de elementos inorgánicos presentes en el aire de la Región Metropolitana 1997–2000. Ministerio de Salud, Laboratorio de Salud Ambiental, Santiago de Chile, 42 p.
- Turnbull, A., Harrison, R., 2000. Major component contribution to PM₁₀ composition in the UK atmosphere. *Atmos. Environ.* 34, 3129–3137.
- UCHile (Universidad de Chile), 1999. Informe País: Estado del Medio Ambiente en Chile. Centro de Análisis de Políticas Públicas, LOM Ediciones, Santiago, Chile, pp. 33–72.