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# Aerosol composition and source apportionment in Santiago de Chile

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**Abstract**

Santiago de Chile, São Paulo and Mexico City are Latin American urban areas that suffer from heavy air pollution. In order to study air pollution in Santiago area, an aerosol source apportionment study was designed to measure ambient aerosol composition and size distribution for two downtown sampling sites in Santiago. The aerosol monitoring stations were operated in Gotuzo and Las Condes during July and August 1996. The study employed stacked filter units (SFU) for aerosol sampling, collecting fine mode aerosol (dp $< 2$ μm) and coarse mode aerosol ($2 <$ dp $< 10$ μm) on polycarbonate filters. Aerosol mass ($PM_{10}$ mass of particles smaller than 10 μm) and black carbon concentration were also measured. Particle-Induced X-ray Emission (PIXE) was used to measure the concentration of 22 trace elements at levels below 0.5 ng $m^{-3}$. Quantitative aerosol source apportionment was performed using Absolute Principal Factor Analysis (APFA). Very high aerosol concentrations were observed (up to 400 $\mu g/m^3$ $PM_{10}$). The main aerosol particle sources in Santiago are resuspended soil dust and traffic emissions. Coarse particles account for 63% of $PM_{10}$ aerosol in Gotuzo and 53% in Las Condes. A major part of this component is resuspended soil dust. In the fine fraction, resuspended soil dust accounts for 15% of fine mass, and the aerosols associated with transportation activities account for a high 64% of the fine particle mass. Sulfate particle is an important component of the aerosol in Santiago, mainly originating from gas-to-particle conversion from $SO_2$. In the Gotuzo site, sulfates are the highest aerosol component, accounting for 64.5% of fine mass. Direct traffic emissions are generally mixed with resuspended soil dust. It is difficult to separate the two components, because the soil dust in downtown Santiago is contaminated with Pb, Br, Cl, and other heavy metals that are also tracers for traffic emissions. Residual oil combustion is observed, with the presence of V, S and Ni. An aerosol components from industrial emissions is also present, with the presence of several heavy metals such as Zn, Cu and others. A factor with molybdenum, arsenic, copper and sulfur was observed frequently, and it results from emissions of copper smelters. © 1999 Elsevier Science B.V. All rights reserved.

*Keywords:* Aerosol; Urban air pollution; Trace elements; Aerosol size distribution; Aerosol source apportionment

## 1. Introduction

The topographical configuration and the geographical location of Santiago de Chile together with an expanding population make the air

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pollution in Santiago severe. A frequent inversion layer adds to this unfavorable condition [1]. Strong enforcement of air pollution reduction by the Chilean Conselho Nacional del Medio Ambiente (CONAMA) includes restriction of automobile circulation and strong industry control. An aerosol source apportionment study was designed to determine the main aerosol sources in the urban area and to check the efficiency of the air pollution control regulations.

Quantitative air pollution studies began in the late 1970s in Santiago. Silo and Lissi [2] correlated S concentrations with visibility in Santiago. Prendéz et al. [3] measured elemental concentrations using high volume aerosol samples, and Trier [4] used a dichotomous sampler to measure $PM_{10}$ and fine and coarse aerosol mass concentrations. Trier and Silva [5] presented seasonal trends of air pollution, and used principal component analysis in order to identify aerosol sources in Santiago. Rojas et al. [1] used single particle analysis and X-ray fluorescence to identify aerosol sources in a site located in the University of Santiago.

In this work, extensive aerosol sampling was performed in two different sites in the urban area of Santiago. At the same site, concentration of trace gases such as CO, $SO_2$ and $NO_x$ were measured. Real time aerosol concentration was monitored using a TEOM real time aerosol mass monitor. Stacked filter unit (SFU) were used to collect fine, coarse and $PM_{10}$ aerosol particles and PIXE analysis was performed in coarse and fine mode filters. The use of receptor modeling such as absolute principal factor analysis identified and quantified aerosol sources for each of the sites. Aerosol size distribution and elemental source profiles were measured in exhaust pipes of buses and cars.

## 2. Aerosol sampling and analysis

Aerosol sampling was performed at two sites during July to September 1996, with a 12 or 24 h sampling time. The sampler was the SFU [6], that uses an inlet that provided a 50% cutoff diameter of 10 μm. The SFU collects coarse mode particles (CPM) ($2.0 < dp < 10$ μm) on a 47-mm-diameter, 8 μm pore size Nuclepore filter while a 0.4 μm pore size Nuclepore filter collects the fine mode particles (FPM) ($dp < 2.0$ μm). The sum of FPM and CPM provides $PM_{10}$ that refers to aerosol particles smaller than 10 μm aerodynamic diameter. The flow rate was typically 17 l/min. Particle bounce was minimized by the use of Apiezon-coated coarse mode filters. The volume was obtained with volume integrators, calibrated with Hastings precision mass flowmeters. Sampling sites were downtown Santiago at the Gotuzo location, and in the Las Condes site, about 8 km from downtown.

Elemental concentrations on the Nuclepore filters were measured with the particle-induced X-ray emission (PIXE) [7] method. The concentrations of up to 22 elements (Al, Si, P, S, Cl, K, Ca, Ti, V, Cr, Mn, Fe, Ni, Cu, Zn, Br, Rb, Sr, Zr, As, Mo and Pb) were determined. A dedicated 5SDH tandem Pelletron accelerator facility, Laboratório de Analise de Materiais por Feixes Iônicos (LAMFI), from the University of São Paulo was used for the PIXE analysis [8]. Detection limits are typically 5 ng $m^{-3}$ for elements in the range $13 < Z < 22$ and 0.4 ng $m^{-3}$ for elements with $Z > 23$. Tow Si(Li) detectors are used in the PIXE system, one optimized for low $Z$ elements and the second has a thick absorber to detect elements heavier than Ca. The arrangement with two Si(Li) detectors provides better detection limits and avoids some of the pile-up and dead time corrections. The two Kevex detectors have 12 μm Be window and 138 eV resolution for the Mn Kα line. Irradiation time was 10 min at a count rate of 2500 cps for the low $Z$ detector and 500–900 cps for the high $Z$ detector. Detection limits were in the range of 0.1–1 ng $m^{-3}$. A large number of NIST and IAEA reference materials were used to check the calibration of the PIXE system. The precision of the elemental concentration measurements is typically in the range of 4–10%. The aerosol mass concentration was obtained through gravimetric analysis. Detection limit for the aerosol mass concentration is about 0.3 μg $m^{-3}$. Precision is estimated at close to 15%. Black carbon (BC) concentration was measured using a reflectance technique. Some effects of light absorption by soil dust particles could interfere with the BC measurements.

To separate the different aerosol components, absolute principal factor analysis (APFA) was used in Ref. [9]. APFA can provide a quantitative elemental source profile, instead of just a qualitative factor-loading matrix as in traditional factor analysis [10]. The absolute elemental source profiles help in the identification of the factors, and can be used to quantitatively compare the factor composition with assumed aerosol sources. The APFA provides the elemental mass contribution of each identified component by calculating the absolute principal factor scores (APFS) for each sample. The source profiles thus obtained can be compared with values from the literature to gain information on enrichment and atmospheric chemistry processes. The measured aerosol mass concentration can be regressed on the APFS to obtain the aerosol total mass source apportionment.

## 3. Results and discussion

The average aerosol mass concentration measured in the two sampling sites is shown in Table 1 as well as the black carbon concentration and ratios between the mass concentrations. The average $PM_{10}$ values measured at Gotuzo are very high (148 μg $m^{-3}$), indicating a severe air pollution problem in downtown Santiago. The values at Las Condes are also high, indicating large geographical spread of the pollution distribution. Black carbon concentration in Gotuzo is 3 times higher than in Las Condes, implying higher traffic load in the Gotuzo sampling site. The last column in Table 1 indicates that traffic emissions at both sites is responsible for a large fraction of the aerosol mass in the fine fraction, since buse and truck emissions are the largest contributor to black carbon in urban areas.

These concentrations can be compared with measurements taken in 1995 at the same Gotuzo sampling site, using the same SFU aerosol sampler and identical methods. The FPM averaged 35.6 μg $m^{-3}$, CPM averaged 73.7 μg $m^{-3}$, while the $PM_{10}$ was 109 μg $m^{-3}$. The 1996 concentration for the aerosol mass is about 30% higher than 1995. This variation can be due to meteorological variability from year to year. Results from other studies show similar values [1,12]. In 1995 the black carbon concentration was a similar value to 1996 at 10.1 μg $m^{-3}$. In a similar study [11] performed downtown in Sao Paulo during the winter of 1997 it was measured an average $PM_{10}$ of 76.6 μg $m^{-3}$, while FPM was at 34.5 μg $m^{-3}$ and CPM was at 42.1 μg $m^{-3}$. These mass concentration values are considerably lower than the ones measured in downtown Santiago. Coarse aerosol mass is also higher than FPM in São Paulo, similar to the situation in downtown Santiago.

The time series of the fine, coarse and $PM_{10}$ aerosol mass concentrations for the Gotuzo sampling site is shown in Fig. 1. A high variability was observed, with $PM_{10}$ concentrations varying from 30 to 430 μg $m^{-3}$. Values in July were higher than in August and September, although a strong air pollution episode was observed around August 27, with $PM_{10}$ values up to 300 μg $m^{-3}$.

The aerosol samples collected in the two stations were analyzed Particle-Induced X-ray Emission (PIXE) for trace elements, by gravimetric analysis for mass concentration and by optical reflectrometry for determination of black carbon concentration. Fig. 2 shows the average elemental

Table 1
Average aerosol mass concentration measured in the two sampling sites, in μg $m^{-3}$, as well as the black carbon concentration[a]

| Sampling sites | IPM (μg/$m^3$) | CPM (μg/$m^3$) | FPM (μg/$m^3$) | BC (μg/$m^3$) | CPM/IPM (%) | FPM/IPM (%) | BC/FPM (%) |
|---|---|---|---|---|---|---|---|
| Gotuzo | 148.4 | 94.0 | 54.4 | 10.4 | 63.3 | 36.7 | 19.0 |
| Las Condes | 76.8 | 41.1 | 35.7 | 3.5 | 53.5 | 46.5 | 9.9 |

[a] IPM – Inhalable particle mass concentration ($PM_{10}$) (particles less than 10 μm) is equal to FPM+CPM; CPM – Coarse mode aerosol mass concentration, particles with diameters $2 < dp < 10$ μm; FPM – Fine mode aerosol mass concentration, with particle diameters $dp < 2$ μm; BC – Black carbon concentration in the fine mode.

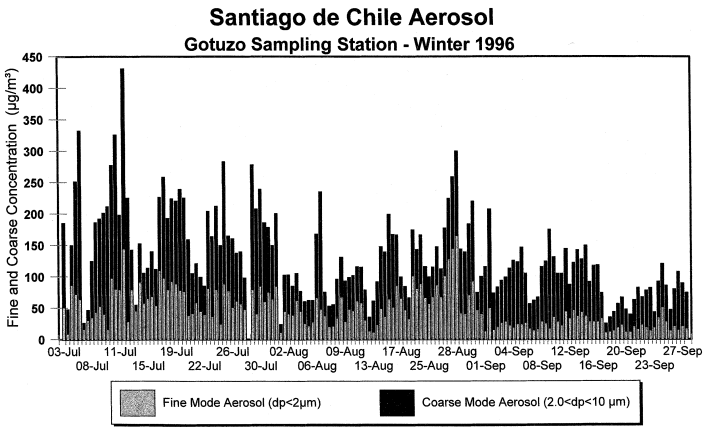


Fig. 1. Aerosol mass concentrations for all individual measurements for the fine, coarse and $PM_{10}$ components for the Gotuzo sampling site.

concentrations for the fine mode aerosol for the two sampling stations. Concentrations of black carbon and sulfur are high and dominate the elemental composition. Fine mode sulfur concentration is similar at the two sites. Iron and soil dust-related elements in the fine mode are high in Gotuzo, due to larger resuspended soil dust. Lead and bromine also show high concentrations in Gotuzo. The presence of molybdenum and tin is unusual for urban aerosols and it is particular to Chile due to the enriched soil for these elements. In the coarse mode, soil dust related elements such as Si, Ca and Fe dominate the elemental mass. Surprisingly high lead and bromine concentrations in the coarse mode aerosol were observed, and indicated that the soil dust in Gotuzo is heavily contaminated with traffic emissions. Also zinc, nickel, copper, arsenic and molybdenum in the coarse mode Gotuzo aerosol presents unusually high concentration.

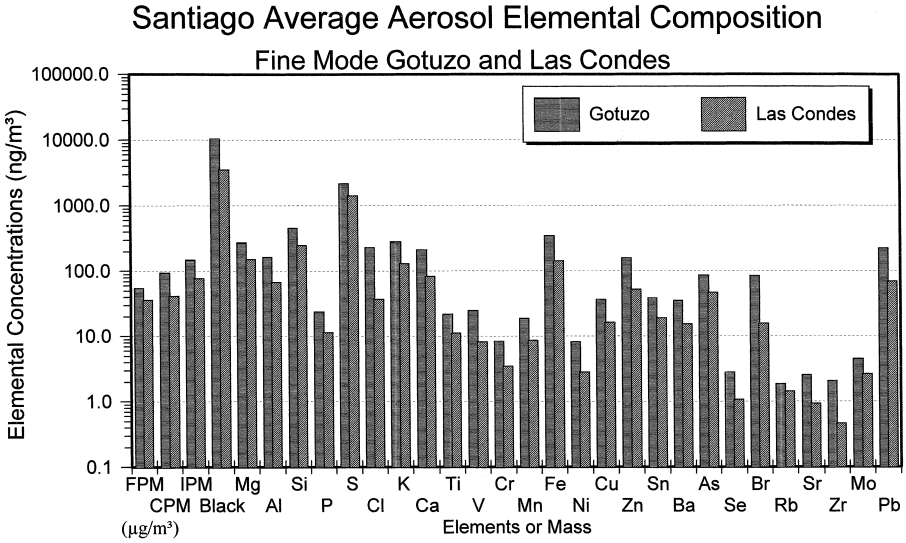


Fig. 2. Average elemental concentration for the fine mode aerosol from Gotuzo and Las Condes sampling stations.

Table 2 shows the VARIMAX rotated factor matrix for the fine mode Gotuzo samples. The values in this matrix represents the associations between each variable and each of the six retained factors. The first factor has high factor loadings for Ca, Al, Si, Ti, Fe, Sr, CPM, Mn, and also some association with Pb, BC, As and P. It represent resuspended soil dust. In Gotuzo the soil dust is contaminated with Pb, as it will be observed latter. The second factor is associated with V, Ni, Zn, Cl and Mn, and represents residual oil combustion. The third factor has high loadings for Br, Pb, Black carbon, K and Sn, representing emissions from the transport sector. Automobile emissions are heavy loaded with Pb and Br, while buses emit essentially black carbon. The factor 4 has high loadings for sulfur, FPM, Se, K and P, representing the sulfate emissions, including secondary aerosol production from the oxidation of $SO_2$. Factor 5 has high loadings for Cu, K and P, representing copper emissions from both long-range transport and also from regional sources. The last factor is loaded with arsenic and sulfur. The last lines from Table 2 show the percentage of original data variability that is explained by each factor. They indicate that the last two factors explain a small part of the original data variability. Fig. 3 shows the quantitative aerosol source apportionment for the Gotuzo fine mode aerosol mass concentration. Sulfates dominate the FPM, while the transport and resuspended soil dust factors account for a significant fraction of the fine mode aerosol mass in Gotuzo. Oil combustion accounts for a small mass (1.01 $\mu g\ m^{-3}$).

Table 3 shows the VARIMAX rotated factor-loading matrix for the fine mode aerosol in Las Condes. Five factors were retained. The first factor represents transport emissions mixed with oil

Table 2
VARIMAX rotated factor loading matrix of the fine mode Gotuzo aerosol[a]

| | Factor 1 Resuspended Soil Dust | Factor 2 Oil Combustion | Factor 3 Transport | Factor 4 Sulfates | Factor 5 Copper | Factor 6 As+S |
|---|---|---|---|---|---|---|
| Ca | 0.92 | 0 | 0.16 | 0 | 0.16 | 0 |
| Al | 0.87 | 0 | 0.34 | 0 | 0.22 | 0 |
| Si | 0.86 | 0 | 0.13 | 0.15 | 0.37 | 0 |
| Ti | 0.86 | 0.23 | 0.26 | 0.19 | 0.11 | 0.10 |
| Fe | 0.85 | 0.35 | 0.14 | 0.23 | 0 | 0.11 |
| Sr | 0.73 | 0.27 | 0.31 | 0.15 | 0.22 | 0.13 |
| CPM | 0.70 | 0 | 0.37 | 0.18 | −0.24 | 0.17 |
| Mn | 0.64 | 0.58 | 0 | 0.31 | 0.10 | 0.14 |
| Zn | 0.30 | 0.87 | 0 | 0.14 | 0 | 0 |
| Cl | 0 | 0.78 | 0.29 | 0.13 | 0.20 | 0 |
| Ni | 0.29 | 0.70 | 0.33 | 0.16 | 0.34 | 0.24 |
| V | 0.26 | 0.65 | 0.31 | 0.22 | 0.36 | 0.24 |
| Br | 0.20 | 0.18 | 0.91 | 0 | 0.20 | 0 |
| Pb | 0.43 | 0.29 | 0.81 | 0.10 | 0.12 | 0 |
| BC | 0.50 | 0.30 | 0.71 | 0.17 | 0.13 | 0.11 |
| Sn | 0.30 | 0.21 | 0.50 | 0.38 | 0.35 | −0.17 |
| S | 0 | 0.19 | −0.11 | 0.81 | 0.21 | 0.33 |
| FPM | 0.32 | 0 | 0.26 | 0.77 | 0 | 0.13 |
| Se | 0.31 | 0.31 | 0.11 | 0.71 | 0.23 | −0.15 |
| Cu | 0.20 | 0.26 | 0.20 | 0.11 | 0.80 | 0 |
| K | 0.25 | 0.36 | 0.43 | 0.42 | 0.56 | 0 |
| P | 0.46 | 0.25 | 0.19 | 0.45 | 0.53 | 0 |
| As | 0.46 | 0 | 0.12 | 0.30 | 0 | 0.72 |
| % Var. | 29.7 | 15.6 | 15.0 | 12.1 | 9.8 | 4.3 |

[a] The total variance explained by the 6 retained factors in Gotuzo is 86.5% of the original data variability.

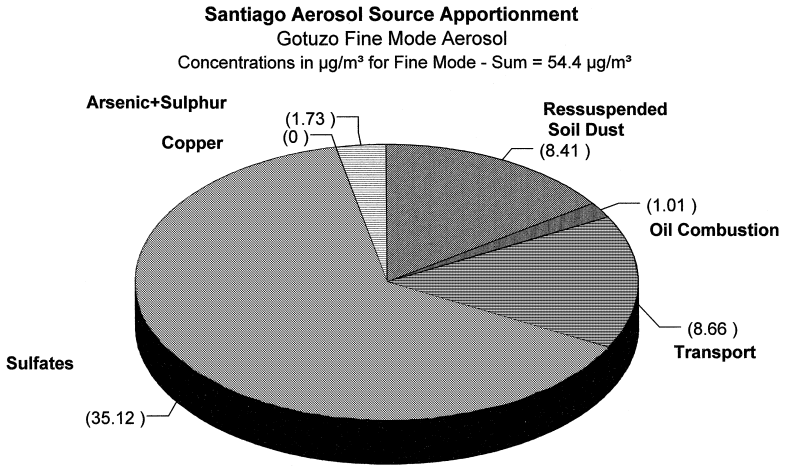


Fig. 3. Quantitative aerosol source apportionment by APFA for Gotuzo fine mode aerosol mass concentration.

combustion and industrial emissions. This mixture on the same factor represents that the fine mode aerosol observed in Las Condes is a very mixed component, downwind of Santiago downtown. The second component represents soil dust, containing heavy metals such as Pb, Br and black

Table 3
VARIMAX rotated factor loading matrix for the fine mode Las Condes aerosol[a]

| Source | Factor 1 Transport | Factor 2 Soil dust | Factor 3 Oil combust. | Factor 4 As+S | Factor 5 Cl+S |
|---|---|---|---|---|---|
| FPM | 0.89 | 0.17 | 0.18 | 0.14 | 0.25 |
| Sn | 0.84 | 0 | 0.27 | 0 | 0 |
| Br | 0.83 | 0.44 | 0.17 | 0 | 0 |
| S | 0.80 | 0 | 0 | 0.39 | 0.36 |
| Se | 0.78 | 0.42 | 0 | 0 | 0.25 |
| K | 0.78 | 0.44 | 0 | 0 | 0.27 |
| BC | 0.75 | 0.50 | 0.27 | 0.15 | 0 |
| Pb | 0.74 | 0.51 | 0.32 | 0.10 | 0 |
| Ni | 0.63 | 0.42 | 0.57 | 0.18 | 0.17 |
| P | 0.60 | 0.43 | 0.10 | 0.51 | 0 |
| V | 0.60 | 0.50 | 0.51 | 0.14 | 0.17 |
| CPM | 0.58 | 0.42 | 0.16 | 0.20 | 0.36 |
| Ca | 0.16 | 0.94 | 0.12 | 0.15 | 0 |
| Al | 0 | 0.91 | 0 | 0 | 0.26 |
| Si | 0.36 | 0.87 | 0 | 0.16 | 0 |
| Ti | 0.25 | 0.86 | 0.18 | 0.23 | 0.20 |
| Fe | 0.35 | 0.84 | 0.32 | 0.19 | 0 |
| Mn | 0.43 | 0.68 | 0.45 | 0.27 | 0 |
| Sr | 0.44 | 0.67 | 0.21 | 0 | 0 |
| Cu | 0.53 | 0.60 | 0.29 | 0.27 | 0 |
| Zn | 0.42 | 0.58 | 0.60 | 0.24 | 0 |
| As | 0 | 0.25 | 0.13 | 0.90 | −0.12 |
| Cl | 0.26 | 0.16 | 0 | −0.11 | 0.91 |
| %Var. | 34.6 | 33.0 | 8.1 | 7.8 | 6.7 |

[a] The total variance explained by the five factors for the fine mode Las Condes aerosol is 90.2% of the original data variability.

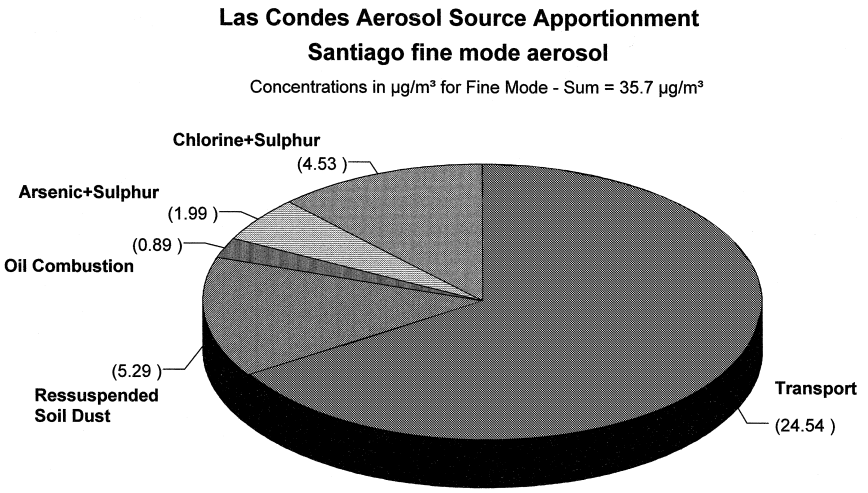


Fig. 4. Quantitative aerosol source apportionment by APFA for the Las Condes fine mode aerosol mass concentration.

carbon, similarly to the Gotuzo situation. The third component represents residual oil combustion with V and Ni. The fourth factor is the As and sulfur factor. The last factor is mostly chlorine, with a small association with sulfur.

Fig. 4 shows the quantitative aerosol source apportionment by APFA for the Las Condes fine mode aerosol mass concentration. The first factor labeled transport is responsible for most of the aerosol fine fraction mass. Resuspended soil dust is the second most important factor. Oil combustion is associated with only 0.98 μg $m^{-3}$ of the fine mode aerosol mass. For the coarse mode aerosol in Las Condes, soil dust accounts for a high 69.5% of the aerosol mass.

## 4. Conclusions

Aerosols produced by the transport activities is the main air pollution problem in Santiago de Chile. Resuspended soil dust, transport and sulfates account for most of the fine and coarse mode aerosol mass in the Santiago air basin. Several quantitative results from this study support this finding. Coarse particles account for 63% of $PM_{10}$ aerosol mass in Gotuzo and 53% in Las Condes. Major part of this component is resuspended soil dust. In the fine fraction, resuspended soil dust accounts for 15.4% of fine mass, and the aerosols associated with transportation activities account for a high 64% of the fine mass. In the Las Condes region, transport accounts for a high fraction of the aerosol loading (69% of fine mass), indicating that in the fine mode, traffic emissions are the major aerosol source.

Sulfate particles are also an important component of the aerosol in Santiago, mainly originating from gas-to-particle conversion from $SO_2$. In Gotuzo, downtown Santiago, sulfates are the highest aerosol component, accounting for 64.5% of fine mass. In the Las Condes sampling site, sulfate variability is included in the traffic component, because of the jointly transport pattern in Santiago. Direct traffic emissions are generally mixed with resuspended soil dust. It is difficult to separate the two components, because the soil dust in downtown Santiago is contaminated with Pb, Br, Cl and other heavy metals. High Pb concentrations were observed in the two sampling sites. Residual oil combustion is always present in the aerosol phase, with the presence of V, Ni and S. In Las Condes the residual oil combustion component accounts for 2.5% of fine mass, while in Gotuzo it accounts for a low 1.9% of fine mass. An aerosol component from industrial emissions is also present, with the participation of several heavy metals such as Zn, Cu and others. A factor with molybdenum, arsenic, copper and sulfur was

observed frequently, although it is responsible for a small fraction of aerosol concentrations. In the coarse mode aerosol in Gotuzo, soil dust accounts for a high 69.5% of coarse aerosol mass, while the factor associated with transport accounts for 27.2%. Other components account for less than 4% of the aerosol coarse mode mass.

The combination of aerosol sampling using SFU, elemental analysis by PIXE and quantitative aerosol source apportionment using APFA showed a very powerful methodology for urban aerosol studies.

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