

Source Apportionment of PM_{10} and $PM_{2.5}$ in Five Chilean Cities Using Factor Analysis

Ilias G. Kavouras and Petros Koutrakis

Environmental Science and Engineering Program, Department of Environmental Health, School of Public Health, Harvard University, Boston, Massachusetts

Francisco Cereceda-Balic

Laboratory of Environmental Chemistry, Department of Chemistry, Universidad Técnica Federico Santa María, Valparaíso, Chile

Pedro Oyola

Comisión Nacional del Medio Ambiente, Region Metropolitana, Santiago de Chile, Chile

ABSTRACT

Chile is a fast-growing country with important industrial activities near urban areas. In this study, the mass and elemental concentrations of PM_{10} and $PM_{2.5}$ were measured in five major Chilean urban areas. Samples of particles with diameter less than $10\ \mu\text{m}$ (PM_{10}) and $2.5\ \mu\text{m}$ ($PM_{2.5}$) were collected in 1998 in Iquique (northern Chile), Valparaíso, Viña del Mar, Rancagua (central Chile), and Temuco (southern Chile). Both PM_{10} and $PM_{2.5}$ annual mean concentrations (PM_{10} : $56.9\text{--}77.6\ \mu\text{g}/\text{m}^3$; $PM_{2.5}$: $22.4\text{--}42.6\ \mu\text{g}/\text{m}^3$) were significantly higher than the corresponding European Union (EU) and U.S. Environmental Protection Agency (EPA) air quality standards. Moreover, the 24-hr PM_{10} and $PM_{2.5}$ U.S. standards were exceeded infrequently for some of the cities (Rancagua and Valparaíso).

IMPLICATIONS

A source apportionment study was conducted in five Chilean cities. Both PM_{10} and $PM_{2.5}$ annual mean concentrations in all five cities were significantly higher than the ambient air quality standards established by the World Health Organization, EU, and the EPA. Consequently, populations residing in these areas are exposed to high particle concentrations that may pose significant health effects. The major sources of coarse particles were soil and sea salt particles. Sources of fine particle mass included automobiles, wood and agricultural waste burning, Cu smelters, and oil refineries. The use of multivariate statistical methods on PM_{10} and $PM_{2.5}$ mass and elemental concentrations provides information on their sources. The results of these studies can be used to assess the risk of air pollution and to develop cost-effective control strategies.

Elements ranging from Mg to Pb were detected in the aerosol samples using X-ray fluorescence (XRF).

For each of the five cities, factor analysis (FA) was applied to identify and quantify the sources of PM_{10} and $PM_{2.5}$. The agreement between calculated and measured mass and elemental concentrations was excellent in most of the cities. Both natural and anthropogenic sources were resolved for all five cities. Soil and sea were the most important contributors to coarse particles ($PM_{10}\text{--}PM_{2.5}$), whereas their contributions to $PM_{2.5}$ were negligible. Emissions from Cu smelters and oil refineries (and/or diesel combustion) were identified as important sources of $PM_{2.5}$, particularly in the industrial cities of Rancagua, Valparaíso, and Viña del Mar. Finally, motor vehicles and wood burning were significant sources of both $PM_{2.5}$ and PM_{10} in most of the cities (wood burning was not identified in Iquique).

INTRODUCTION

A large number of air pollution health effects studies conducted in North America and western European cities have reported associations between daily mortality and morbidity outcomes and particle concentrations.¹⁻⁹ For this reason, particle exposures have been characterized in many urban areas in the United States and Europe.¹⁰⁻¹³ However, a limited number of studies on the composition and health effects of ambient particles have been conducted in developing countries.¹⁴⁻¹⁷

Chile is one of the most urbanized and industrialized countries in South America, with 86% of the population residing in large cities. Chile's economy is based mainly on the export of mineral and agricultural products. Industry

is concentrated primarily in and around five main urban centers: Santiago de Chile, Valparaíso, Concepcion, Rancagua, and Valdivia. Most of the particle composition and health effects studies have been conducted in the Santiago metropolitan area.¹⁷⁻²⁰ These studies suggested that concentration levels of particle mass, elements, and organic compounds were elevated, and daily respiratory-related emergency visits were correlated with ambient PM₁₀ and PM_{2.5} concentrations.¹⁷⁻²⁰ In an effort to investigate the impacts of industrial activities and vehicular emissions on a number of Chilean urban environments other than Santiago, the Comisión Nacional del Medio Ambiente has undertaken an ambitious air quality program in five cities: Temuco, Rancagua, Viña del Mar, Valparaíso, and Iquique. In this paper, we present the results of the source apportionment analysis of PM₁₀ and PM_{2.5} samples collected as a part of the five-city measurement program.

METHODS

Sampling Sites

A map of Chile illustrating the five cities (Temuco, Rancagua, Valparaíso, Viña del Mar, and Iquique) is shown in Figure 1. Temuco (population 210,000) is located ~800 km south of Santiago de Chile and 200 km north of the industrial city of Valdivia. Public services and agriculture comprise the major occupations, and no industrial activity occurs in this area. Rancagua (population 180,000) is located ~120 km south of Santiago de Chile. It is a busy commercial center as a result of mining and agricultural industries. A large Cu smelter is located ~30 km east of the city at the beginning of the Andes (see Figure 1).

Valparaíso is one of Chile's largest cities with 1,275,000 inhabitants. It is a major seaport and manufacturing center of items including processed food, textiles, paint, chemicals, and metal products. Viña del Mar is a coastal city located north of Valparaíso (see Figure 1). The population of Viña del Mar comprises ~1,000,000 inhabitants. It is one of the leading resort communities of the country and one of the major seaside resorts in South America. The city is also a manufacturing center. Major industrial units such as an oil refinery, a Cu smelter, and electric power plants are located north of Valparaíso and Viña del Mar.

Iquique is located in northern Chile near the ocean and west of Atacama Desert (see Figure 1). The population of this city is ~145,000. Iquique is also a major seaport of Chile and serves as the outlet for the surrounding area, which is rich in nitrates, iodine, salt, and guano. The chief industries include fish canning, sugar refining, and cement manufacturing. Rock and sand enclose the city on the landward side.



Figure 1. Map of Chile with the five cities.

Sampling and Analysis Techniques

Both PM_{2.5} (particles with aerodynamic diam $d_p < 2.5 \mu\text{m}$) and PM₁₀ (particles with aerodynamic diam $d_p < 10 \mu\text{m}$) samples were collected in the five Chilean cities. Twenty-four-hour samples were collected using the Harvard Impactor.²¹ The frequency of sampling was every fourth day during the calendar year of 1998. The PM_{2.5} and PM₁₀ mass measurements were conducted using gravimetric analysis. Also, elemental analysis was conducted using X-ray fluorescence (XRF) at the Desert Research Institute, Reno, NV.²²

To minimize analytical costs, a subset of the collected filters, ~750, was analyzed. Forty PM_{2.5} and PM₁₀ filter samples (1 sample every 12 days; ~10 samples per season) for each of the five cities were selected. As shown below,

40 samples per site were sufficient to conduct factor analysis (FA). Based on the fraction of concentrations above the detection limit for each of the analyzed elements, they were classified in three categories: (1) for Al, Si, S, K, Ca, Ti, Mn, Fe, Cu, Zn, Br, Sr, and Pb, 95% of the measurements were above the detection limit; (2) for Zr, Mg, Rb, V, Cl, As, Ba, Mo, Cr, and Ni, the percentages were between 75 and 95%; and (3) for Yt, Cd, Sn, Co, Sb, P, Se, La, Tl, Pd, Ag, In, Ga, Au, Hg, and U, the percentages were below 75%. The third group was excluded from the entire data analysis and the second group was excluded only for the source apportionment analysis. However, in some cases, elements such as Zr, V, Ni, Cr, As, and Mg were included in the FA because their ambient levels were high in a specific city and they were tracers of sources such as oil refineries, metal processing industries, and Cu smelters.

Statistical Techniques

Over the last two decades, FA has been widely used to identify sources of ambient particles.²³⁻²⁷ FA was applied to 10 data sets [five cities, two particle fractions each (PM₁₀ and PM_{2.5})]. The elemental concentration matrix $[X(nxm)]$ with n rows (the number of analyzed species) and m columns (the number of samples analyzed) was standardized using the Z-score. The Z-score of each element for every sample was determined using the following formula:

$$Z_{ik} = \frac{C_{ik} - \bar{C}_i}{\sigma_i} \quad (1)$$

where $I = 1, 2, \dots, n$ is the number of analyzed elements; $k = 1, 2, \dots, m$ is the number of samples; Z_{ik} is the standardized value of the element i for the sample k ; C_{ik} is the concentration of the element i for the sample k ; \bar{C}_i is the mean concentration of the element i ; and σ_i is the standard deviation of the i -th element concentration distribution. FA proceeds through the determination of the eigenvector-factor $B(nxn)$ and the corresponding transpose $B^{-1}(nxn)$ matrices, which are used to calculate a diagonal table $\Lambda(nxn)$ using the following equation:

$$B(nxm) \cdot C(nxn) \cdot B^{-1}(nxn) = \Lambda(nxn) \quad (2)$$

where $C(nxn)$ is the correlation matrix. The matrix $\Lambda(nxn)$ contains the eigenvalues of the corresponding eigenvectors-factors. Although n factors are initially extracted to explain the total variance of the system, a limited number of p factors accounted for more than 90% of the variance. Consequently, the dimensions of both the eigenvector $[B(nxn)]$ and eigenvalues $[\Lambda(nxn)]$ matrices were reduced to (pxn) .

However, FA cannot be used alone to quantify the sources of ambient aerosol, because the solution it yields is one of an infinite number of mathematically equivalent

solutions. Even supposing that the predicted source contributions estimated by the model are nonnegative, a great number of solutions are still possible. To clarify the meaning of these factors, they were rotated. Although the factor loadings have been changed, the factor solutions are mathematically equivalent. Orthogonal and oblique rotations can be used. In oblique rotations, the factor vectors can take any position in space that allows more freedom than in the case of orthogonal rotations. The cosine of the angle between the factor axes indicates the correlation between the rotated factors (SPSS Version 8.0, Chicago, IL).

The factor matrix, $FS(pxm)$, is the product of the coefficient matrix of the variables $[W(pxn)]$ and the Z-score matrix $[Z(nxm)]$, as follows:

$$FS(pxm) = W(pxn) \cdot Z(nxm) \quad (3)$$

where

$$B(pxm) = W(pxn) \cdot \lambda_i \quad (4)$$

and λ_i is the eigenvalue of factor (source) P . Because these factor scores (FS) are calculated from the average normalized elemental concentrations, they have a mean value of 0 and a standard deviation of 1. To determine the real FS (source contributions), the "absolute zero FS" were calculated.²⁵ This was achieved by separately scoring an extra day where ambient concentrations of elements were set at 0. The Z-score for this "extra day" is calculated as follows:

$$(Z_0)_i = \frac{0 - \bar{C}_i}{\sigma_i} \quad (5)$$

Using the following equation, the absolute zero factor scores (FS^*_0) were calculated as follows:

$$FS^*_0(px1) = W(pxn) \cdot Z_0(nx1) \quad (6)$$

The absolute FS (AFS*) for each day can be calculated using eq 7

$$AFS^*(pxm) = FS(pxm) - FS^*_0(pxm) \quad (7)$$

The source contributions can be estimated by regressing daily mass and elemental concentrations on AFS*.

$$M_k = a + \sum_{j=1}^p a_j (AFS^*)_{jk} \quad (8)$$

where M_k is the particle-associated mass or elemental concentration (in ng/m³) for the sample k , AFS^*_{jk} is the rotated absolute factor score of source j in sample k , a_j is the regression coefficient of the AFS^*_{jk} to mass or elemental

concentration, and a is the unexplained. The agreement between the calculated and estimated mass and elemental concentrations was examined by the percent root mean square error, which is defined as follows:

$$\%RMSE = \frac{|M_{\text{measured}} - M_{\text{estimated}}|}{M_{\text{measured}}} \times 100 \quad (9)$$

RESULTS AND DISCUSSION

PM₁₀ and PM_{2.5} Mass Concentrations

The arithmetic annual mean and standard deviation of PM₁₀ and PM_{2.5} mass concentrations in the five Chilean cities are presented in Table 1. The PM₁₀ mean annual mass concentrations for all cities were 10–50% higher than the PM₁₀ standards set by the European Union (EU) (30 µg/m³) and the U.S. Environmental Protection Agency (EPA) (50 µg/m³).^{28,29} The U.S. 24-hr PM₁₀ National Ambient Air Quality Standard (NAAQS) was exceeded from 1 to 8 times in these cities (Temuco 3, Rancagua 8, Valparaíso 6, Viña del Mar 1, and Iquique 6). The PM₁₀ mean mass concentration was highest in Valparaíso (77.5 ± 2.7 µg/m³) and Rancagua (73.8 ± 4.2 µg/m³) (see Table 1). Although Viña del Mar is located between the industrial area and Valparaíso, the PM₁₀ mass annual mean concentration was 55.5 ± 3.5 µg/m³ (see Table 1). Viña del Mar is located in a gulf (see Figure 1); thus, the impact of transported emissions from the local industries on this city was less pronounced. Higher PM₁₀ mass concentrations have been measured in the metropolitan area of Santiago de Chile, which is more polluted (cold period 123.9 µg/m³; warm period 80.3 µg/m³) than the other five Chilean cities.¹⁷ PM₁₀ mass concentration levels in the five Chilean cities were much higher than those measured in North American urban environments (Halifax 25.6 µg/m³, Montreal 27.8 µg/m³, Quebec City 23.5 µg/m³, Ottawa 22.6 µg/m³, Toronto 28.1 µg/m³, Calgary 26.8 µg/m³, Vancouver 26.9 µg/m³, Memphis, TN 30.9 µg/m³, Muhlenberg, KY 23.4 µg/m³, Long Beach, CA 37–41 µg/m³, Boston, MA 18–20 µg/m³, Washington, DC 28 µg/m³, Philadelphia, PA 26 µg/m³, and Mexico City 115 µg/m³).^{30,32}

Table 1. PM₁₀ and PM_{2.5} annual mean mass concentrations [±SE (standard error)] of the five Chilean cities.

Urban Area	Mean Annual Concentrations	
	PM ₁₀ (µg/m ³)	PM _{2.5} (µg/m ³)
	Mean ± SE	Mean ± SE
Temuco	67.7 ± 3.2	35.2 ± 2.6
Rancagua	73.8 ± 4.2	42.6 ± 3.3
Viña del Mar	55.5 ± 3.5	19.8 ± 2.4
Valparaíso	77.5 ± 2.7	35.7 ± 1.8
Iquique	62.1 ± 3.5	24.7 ± 1.2

The PM_{2.5} annual mean mass concentrations measured in the five Chilean cities were also higher than the U.S. PM_{2.5} annual standard (15 µg/m³) (see Table 1). Higher PM_{2.5} mass concentration levels were measured in Rancagua (42.6 ± 3.3 µg/m³), which was more industrialized than the other cities (see Table 1). Although there were no major industrial activities, PM_{2.5} mass concentrations were higher in Temuco and Iquique (35.3 ± 2.6 and 35.9 ± 1.2 µg/m³, respectively) than in Valparaíso (36.3 ± 1.8 µg/m³) and Viña del Mar (23.4 ± 2.4 µg/m³) (see Table 1). The 24-hr PM_{2.5} NAAQS of 65 µg/m³ was exceeded 7 times in Rancagua, 4 times in Temuco, and once in Viña del Mar. The PM_{2.5} mass mean concentrations measured in the five Chilean cities (see Table 1) were significantly higher than those measured in major urban and industrial areas throughout western Europe and North America (Halifax 14.1 µg/m³, Montreal 15.9 µg/m³, Quebec City 11.9 µg/m³, Ottawa 12.6 µg/m³, Toronto 16.8 µg/m³, Calgary 11.2 µg/m³, Vancouver 15.5 µg/m³, Memphis 21.3 µg/m³, Muhlenberg 14.6 µg/m³, Bakersfield, CA 18.4 µg/m³, Boston 15.2 µg/m³, Chicago, IL 16.8 µg/m³, Dallas, TX 11.7 µg/m³, Philadelphia 21.1 µg/m³, Phoenix, AZ 22.5 µg/m³, Riverside, CA 18.4 µg/m³, and downtown Los Angeles, CA 11.9–28.8 µg/m³),^{30,32,33} but lower than those measured in metropolitan Santiago de Chile (cold period 71.3 µg/m³; warm period 34.3 µg/m³).¹⁷ These results suggest that populations living in these urban centers are exposed to high concentration levels of PM₁₀ and PM_{2.5} particles, which can cause significant health effects.¹⁻¹³

Source Apportionment

Tables 2–6 present the results of the FA. For all data sets, the retained factors explained more than 90% of the variance. Figures 2a–2j present a comparison between the measured and calculated PM₁₀ and PM_{2.5} mass concentrations for Temuco (a, b), Rancagua (c, d), Viña del Mar (e, f), Valparaíso (g, h), and Iquique (i, j). In addition, the percent contribution of each source in both PM_{2.5} and PM₁₀ for Temuco, Rancagua, Viña del Mar, Valparaíso, and Iquique are shown in Figures 3a and 3b, respectively.

For each of the 10 analyzed data sets, a limited number of elements was included in the FA. These elements were mostly tracers of the different suspected particle sources. A limited number of elements, ~10, was used because of the insufficient number of observations for each data set, ~40. Therefore, the use of less than 10 variables was necessary to obtain enough degrees of freedom for the FA. The rest of the elements were apportioned by regressing their daily concentrations against the daily AFS. The identification of the determined factors was achieved by examining the factor loadings of the source tracer elements in each of the factors. In particular, Al, Si, and Ca were used as soil tracers. This was supported by the Al/Si

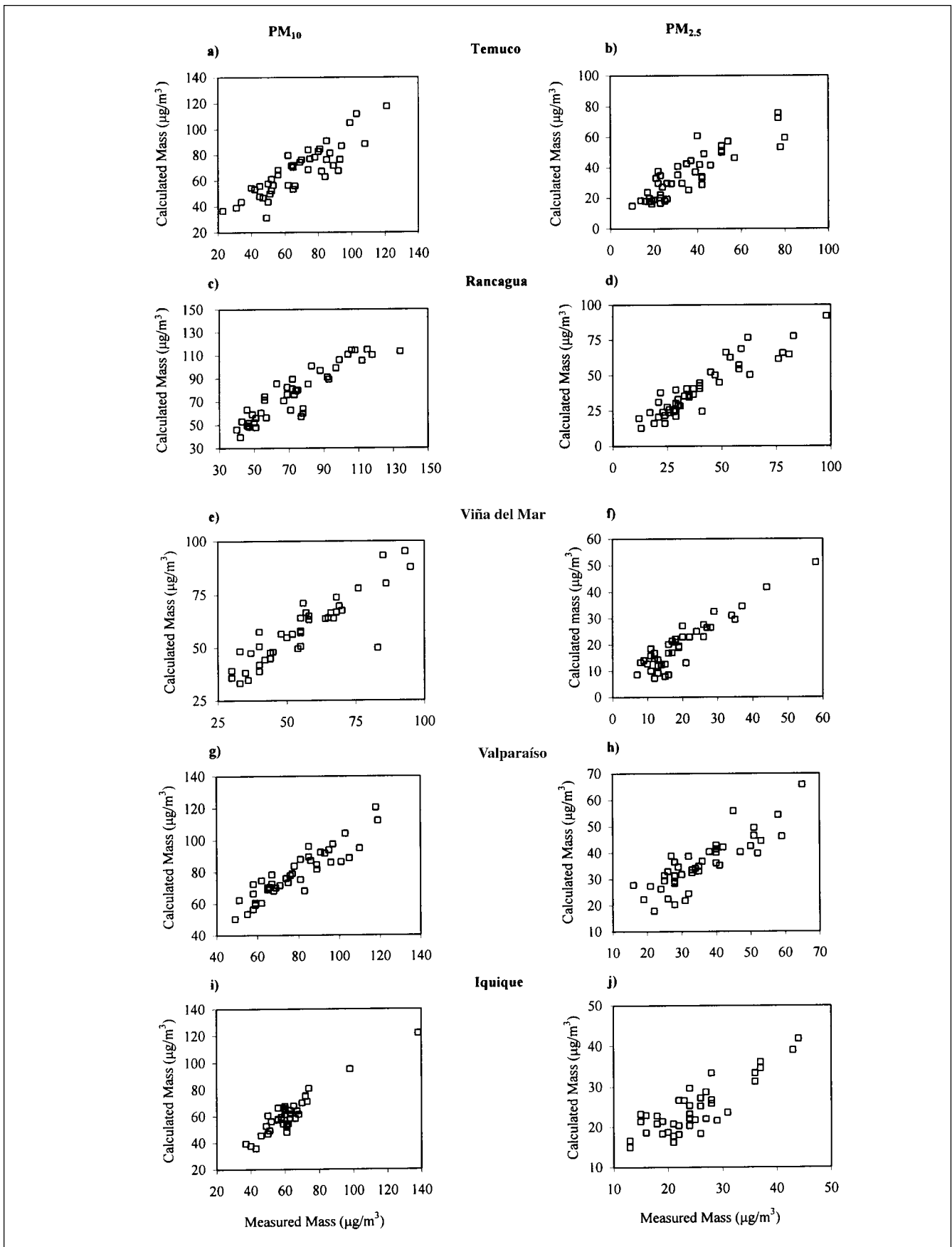


Figure 2. Comparison of measured and calculated mass concentrations of PM_{10} and $PM_{2.5}$ in (a, b) Temuco, (c, d) Rancagua, (e, f) Viña del Mar, (g, h) Valparaíso, and (i, j) Iquique.

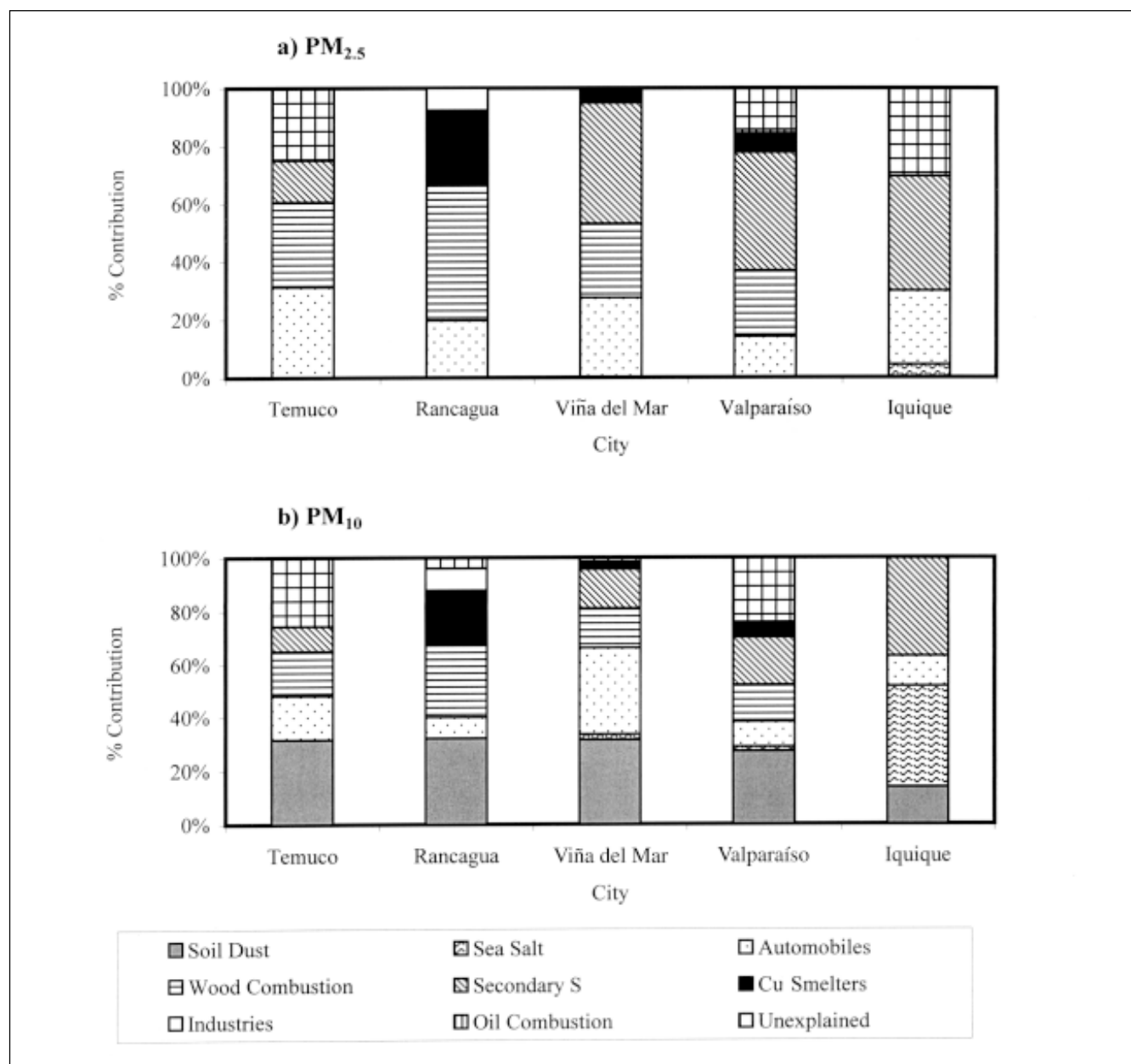


Figure 3. Percent source contributions to (a) PM_{2.5} and (b) PM₁₀ mass in Temuco, Rancagua, Viña del Mar, Valparaíso, and Iquique.

(0.39 ± 0.07 for PM₁₀ and 0.38 ± 0.18 for PM_{2.5}) and Ca/Si (0.38 ± 0.04 for PM₁₀ and 0.64 ± 0.07 for PM_{2.5}) ratios. The sea factor was identified using Cl. Both Br and Pb were used as tracers of vehicular emissions, which was further supported by the Br/Pb ratios (0.33 ± 0.06). Oil combustion and refining (in Valparaíso and Viña del Mar) were resolved using Ni and V. Indeed, the Ni/V ratios (0.36 ± 0.01 for PM₁₀ and 0.38 ± 0.03 for PM_{2.5}) were similar to those calculated for oil combustion and refining. Potassium was originated from both soil and wood burning.

Cu, As, and Zn were primarily used to identify emissions from Cu smelters located in the vicinity of Rancagua, Valparaíso, and Viña del Mar.^{34,35} Indeed, the concentrations of these elements were much higher in Rancagua,

Valparaíso, and Viña del Mar than those measured in Temuco and Iquique. It was previously reported that gaseous SO₂ is the major form of sulfur emitted by Cu smelters in Chile;^{34,35} hence, sulfur was also included in the FA. However, a separate factor associated with sulfur was resolved at Temuco, Valparaíso, Viña del Mar, and Iquique. This factor was attributed to secondary sulfur produced through the oxidation of SO₂, which can be emitted from Cu smelters, oil combustion and refining, automobile emissions, and other combustion-related processes. Elements such as Zr and Cr were used to resolve the contribution of mechanical processing plants located in Rancagua. Next, we present the source apportionment results by city.

Table 2. Source contributions to PM₁₀ and PM_{2.5} mass (μg/m³) and elemental (ng/m³) concentrations in Temuco.

	Motor Vehicle	Soil	Sulfur Source	Wood Burning	Calculated Mass	Measured Mass	%RMSE
PM₁₀							
Mass	17.1	19.2	5.8	10.1	52.2	67.7	14.6
Mg	-	63	-	-	63	115	27.3
Al	-	2817	-	-	2817	2737	3.9
Si	-	5538	-	54	5592	5787	3.6
P	-	30	-	6	36	20	60.3
S	-	-	616	21	637	636	1.2
K	235	249	87	337	908	893	11.6
Ca	148	1153	30	-	1331	1397	20.2
Ti	-	154	-	4	158	157	7.9
V	-	3	-	-	3	4	56.4
Cr	-	-	0	-	0	1	44.2
Mn	5	39	-	1	46	43	7.3
Fe	238	1588	-	-	1826	1786	4.0
Co	-	9	-	-	9	9	48.1
Cu	6	4	-	-	10	15	17.6
Zn	29	16	4	6	56	62	17.9
As	-	-	7	-	7	4	45.9
Br	94	-	-	-	94	96	5.2
Rb	0	0	0	1	2	2	17.1
Sr	5	10	-	-	15	15	14.7
Zr	-	4	-	-	4	3	21.2
Pb	272	8	22	9	312	311	2.9
PM_{2.5}							
Mass	10.9	-	5.0	10.3	26.2	35.3	20.0
Mg	-	2	-	-	2	28	34.9
Al	-	90	-	-	90	92	9.6
Si	-	196	-	-	196	188	11.8
P	-	1	1	0	3	5	39.6
S	-	-	556	-	556	567	7.0
K	201	-	87	227	515	513	15.4
Ca	-	67	-	-	67	81	23.3
Mn	3	2	-	-	6	4	31.4
Fe	44	96	-	-	140	132	13.0
Cu	2	-	1	0	3	4	41.6
Zn	15	-	4	6	26	29	22.0
Br	72	-	-	-	72	67	12.7
Rb	0	-	0	1	1	2	21.4
Sr	0	1	-	-	1	1	29.2
Pb	223	-	29	-	252	252	6.6

Temuco. Four factors were retained from the source apportionment analysis of PM₁₀ and PM_{2.5} in Temuco. The identified sources were automobile emissions, soil, sulfur, and wood combustion emissions, which explained 98.6 and 93.8% of the total variance of PM₁₀ and PM_{2.5} data sets, respectively. The contributions of each source

to the PM₁₀ and PM_{2.5} mass and elemental concentrations are presented in Table 2. Overall, there was good agreement between the measured and calculated PM₁₀ and PM_{2.5} mass, as shown in Figures 2a and 2b; however, a relatively significant mass concentration ($15.5 \pm 2.3 \mu\text{g}/\text{m}^3$ for PM₁₀ and $9.1 \pm 2.3 \mu\text{g}/\text{m}^3$ for PM_{2.5}) was not attributed to these factors. This unexplained mass may be attributed to the presence of forests around the city and other local activities that were not identified by the FA. Organic compounds can be emitted directly from both higher terrestrial plants (biogenic) and manmade combustion processes. In addition, secondary organic particles can be formed by the condensation of low vapor pressure organic molecules, which were photochemically produced from biogenic volatile organic compounds.³⁶

Motor vehicles were the predominant source of Br and Pb (see Table 2). Vehicular emissions accounted for ~10.9 μg/m³ of PM_{2.5} mass and 17.1 μg/m³ of PM₁₀ mass (see Table 2). These contributions represented 25.2% of PM₁₀ and 30.8% of PM_{2.5} (see Figures 3a and 3b). The presence of K, Rb, Ca, Fe, Mn, Zn, and Sr in this factor is the result of the correlation of automobile contribution with those of other local sources. As mentioned earlier, Temuco is located in a valley surrounded by hills (~500 m) where frequent formation of temperature inversions take place. Consequently, particles emitted from automobiles, wood combustion, and other sources can mix.

Soil was also identified as a source of airborne particles in both PM₁₀ and PM_{2.5}. Al, Si, Ca, Ti, Fe, and Sr were associated with soil in both fractions. Although soil was

Soil was also identified as a source of airborne particles in both PM₁₀ and PM_{2.5}. Al, Si, Ca, Ti, Fe, and Sr were associated with soil in both fractions. Although soil was

Table 3. Source contributions to PM₁₀ and PM_{2.5} mass ($\mu\text{g}/\text{m}^3$) and elemental (ng/m^3) concentrations in Rancagua.

	Motor Vehicle	Soil	Mechanical Industries	Wood Burning	Cu Smelters	Calculated Mass	Measured Mass	% RMSE
PM₁₀								
Mass	5.9	23.7	6.0	20.3	14.9	70.8	73.9	12.1
Mg	-	138	10	-	-	148	171	22.5
Al	-	3544	-	-	-	3544	3555	3.1
Si	-	8580	-	-	-	8580	9241	4.4
S	-	-	-	45	1526	1571	1530	13.7
K	29	800	-	415	26	1270	1275	5.6
Ca	-	2048	-	549	-	2597	2968	29.7
Ti	-	128	13	-	-	140	159	14.5
V	2	5	-	-	-	7	9	39.1
Cr	-	-	21	-	-	21	22	25.3
Mn	-	38	44	1	-	84	101	18.4
Fe	97	1347	462	81	-	1987	2307	9.3
Co	-	-	4	-	-	4	10	46.4
Ni	1	2	-	-	-	3	3	42.7
Cu	9	-	-	-	57	66	89	38.5
Zn	11	6	4	-	24	46	89	25.5
As	13	-	-	-	79	92	100	34.0
Br	68	-	-	10	-	78	79	39.6
Rb	-	2	-	1	-	3	4	12.9
Sr	-	10	1	-	-	12	15	13.1
Zr	-	3	23	-	-	26	21	27.1
Mo	3	-	4	-	2	9	14	35.4
Pb	220	12	-	43	28	303	309	26.9
PM_{2.5}								
Mass	8.5	-	3.3	20.2	11.0	43.0	42.6	15.6
Mg	-	26	6	-	-	33	43	32.1
Al	-	290	-	-	-	290	278	8.5
Si	-	856	-	-	-	856	894	5.9
S	-	-	-	50	1613	1662	1675	12.4
K	26	71	-	405	21	524	639	9.5
Ca	-	376	-	93	-	468	536	29.1
Ti	-	26	12	-	-	38	34	30.8
V	1	6	-	-	-	7	7	43.6
Cr	-	-	7	-	-	7	9	18.3
Mn	-	10	22	-	10	41	46	30.9
Fe	32	329	90	-	-	452	580	14.7
Co	-	-	1	-	-	1	3	40.6
Ni	1	2	-	-	-	2	3	39.9
Cu	7	-	-	-	24	31	32	35.3
Zn	10	-	4	-	30	43	60	31.5
As	10	-	-	-	98	108	114	32.4
Br	55	-	-	7	-	62	63	17.2
Rb	-	1	-	1	-	1	2	27.0
Sr	-	2	-	-	-	2	3	25.4
Zr	-	-	5	-	-	5	5	33.7
Mo	1	-	1	-	5	7	8	36.9
Pb	212	4	-	45	26	287	291	20.4

Table 4. Source contributions to PM₁₀ and PM_{2.5} mass ($\mu\text{g}/\text{m}^3$) and elemental (ng/m^3) concentrations in Viña del Mar.

	Cu Smelter	Oil Combustion	Soil	Motor Vehicle	Wood Burning	Sulfur Source	Sea Salt	Calculated Mass	Measured Mass	% RMSE
PM₁₀										
Mass	1.5	0.1	18.2	19.0	8.6	8.4	1.2	57.1	55.5	11.3
Mg	-	-	85	-	-	-	47	131	156	20.6
Al	-	-	2407	185	-	-	-	2591	2589	3.2
Si	-	-	5618	572	-	-	-	6191	6009	3.4
S	-	-	-	-	-	2084	-	2084	1855	11.2
Cl	-	-	-	-	-	-	2215	2215	2284	18.1
K	-	-	499	64	189	-	-	751	749	2.8
Ca	-	-	1250	-	-	-	-	1250	1285	18.0
Ti	-	-	139	-	-	-	-	139	133	14.8
V	-	21	-	-	-	2	-	23	29	27.9
Cr	-	-	4	-	-	-	-	4	4	33.0
Mn	1	-	28	-	-	-	-	29	32	13.1
Fe	42	-	1273	244	123	-	-	1682	1703	8.1
Ni	-	8	-	-	-	2	-	10	10	147.8
Cu	42	-	-	-	-	8	-	49	58	21.0
Zn	120	-	89	-	-	86	-	295	289	35.1
As	23	-	-	-	-	-	-	23	33	37.6
Br	-	-	1	24	-	-	0	25	26	2.5
Rb	-	-	3	-	0	-	-	3	3	14.9
Sr	0	-	6	2	0	-	1	9	8	8.8
Zr	0	-	2	-	-	-	-	2	2	22.7
Mo	2	-	-	-	-	-	-	2	3	32.9
Sn	-	-	3	-	-	-	-	3	3	57.6
Sb	-	-	1	-	-	-	-	1	3	43.8
Ba	-	-	27	21	-	-	-	47	46	32.0
Pb	50	(1)	-	59	-	40	-	148	138	10.4
PM_{2.5}										
Mass	0.9	0.2	-	6.0	5.6	9.1	n.r.	21.8	19.9	21.5
Mg	-	-	127	-	-	-	n.r.	127	36	64.6
Al	-	-	74	-	-	-	n.r.	74	72	10.2
Si	-	-	175	-	-	-	n.r.	175	201	13.3
S	-	-	-	-	-	1740	n.r.	1740	1725	10.1
K	6	3	17	18	128	-	n.r.	171	183	4.8
Ca	-	-	103	-	-	-	n.r.	103	90	29.0
Ti	-	-	8	-	-	-	n.r.	8	10	52.5
V	-	14	-	-	-	5	n.r.	19	20	34.6
Mn	0	-	2	-	-	-	n.r.	2	4	32.5
Fe	3	7	81	25	17	8	n.r.	141	162	18.0
Ni	-	5	-	-	-	1	n.r.	6	7	26.7
Cu	28	-	-	-	-	4	n.r.	32	30	32.1
Zn	89	-	28	-	-	57	n.r.	174	192	35.6
As	29	-	-	-	-	-	n.r.	29	29	38.8
Br	-	-	-	13	1	-	n.r.	13	13	4.8
Rb	-	-	-	-	0	-	n.r.	0	0	26.6
Sr	-	-	0	-	-	-	n.r.	0	1	28.9
Mo	2	-	-	-	-	-	n.r.	2	2	48.9
Pb	55	1	-	32	-	24	n.r.	113	111	10.7

Table 5. Source contributions to PM₁₀ and PM_{2.5} mass ($\mu\text{g}/\text{m}^3$) and elemental (ng/m^3) concentrations in Valparaíso.

	Cu Smelters	Sulfur Source	Motor Vehicles	Oil Combustion	Wood Burning	Soil	Sea Salt	Calculated Mass	Measured Mass	% RMSE
PM₁₀										
Mass	4.1	14.0	7.3	0.3	10.9	21.0	1.2	58.8	77.6	7.6
Mg	-	-	-	-	-	94	85	178	216	15.3
Al	-	-	-	-	-	2292	-	2292	2285	5.6
Si	-	-	-	-	-	5184	-	5184	5565	7.8
S	-	1994	-	15	-	-	-	2009	1911	8.0
Cl	-	-	-	-	-	-	3208	3208	3479	9.8
K	12	-	40	14	241	487	-	794	799	1.8
Ca	-	-	334	-	145	1194	-	1672	1908	19.7
Ti	-	-	9	-	-	120	-	129	116	10.3
V	-	-	-	12	-	3	-	15	18	17.6
Cr	4	-	-	0	-	-	-	4	3	47.2
Mn	6	-	-	-	-	26	-	32	49	35.0
Fe	387	-	-	-	-	1396	-	1783	2236	14.1
Ni	-	-	-	4	-	0	-	4	6	20.6
Cu	108	-	-	-	-	61	-	169	156	31.3
Zn	285	149	-	77	-	-	-	511	453	31.4
As	1	45	-	-	-	-	-	46	73	34.3
Br	-	-	52	-	4	-	-	56	59	6.2
Rb	-	-	-	-	0	2	-	3	2	42.6
Sr	-	-	1	-	-	8	-	9	13	18.7
Zr	0	-	-	-	-	2	-	2	3	23.6
Mo	3	-	-	-	-	2	-	5	5	40.1
Sn	1	-	-	-	-	3	-	4	6	27.5
Sb	1	-	-	-	-	-	-	1	8	32.6
Ba	3	-	23	-	-	28	-	54	94	20.3
Pb	55	69	138	21	-	-	-	284	295	9.0
PM_{2.5}										
Mass	2.3	14.7	5.0	0.4	8.1	0.1	n.r.	30.6	35.7	14.6
Mg	-	-	-	-	-	13	n.r.	13	45	28.9
Al	-	-	-	-	-	95	n.r.	95	76	16.0
Si	-	-	-	-	-	245	n.r.	245	237	12.5
S	-	1916	-	-	-	-	n.r.	1916	1805	5.7
K	2	-	-	-	218	-	n.r.	221	258	5.8
Ca	-	-	-	-	-	141	n.r.	141	137	17.2
Ti	-	-	-	-	-	10	n.r.	10	11	21.6
V	-	-	-	13	-	-	n.r.	13	13	18.6
Mn	-	3	-	-	-	3	n.r.	5	8	34.6
Fe	33	-	-	-	-	161	n.r.	194	233	25.5
Ni	-	-	-	4	-	-	n.r.	4	5	15.1
Cu	49	-	-	-	-	1	n.r.	51	50	21.8
Zn	232	80	-	49	-	-	n.r.	361	247	28.1
As	24	36	-	-	-	-	n.r.	60	34	30.4
Br	-	-	33	-	-	-	n.r.	33	31	7.4
Sr	-	-	-	-	-	1	n.r.	1	1	28.2
Ba	-	-	-	-	-	6	n.r.	6	20	34.6
Pb	101	38	103	20	-	-	n.r.	262	236	13.0

Table 6. Source contributions to PM₁₀ and PM_{2.5} mass (μg/m³) and elemental (ng/m³) concentrations in Iquique.

	Motor Vehicle	Sea Salt	Soil	Sulfur Source	Calculated Mass	Measured Mass	% RMSE
PM₁₀							
Mass	7.2	23.8	8.6	23.2	62.9	62.1	7.5
Mg	20	316	13	-	349	381	6.7
Al	-	-	501	-	501	578	14.0
Si	-	-	1915	-	1915	2023	6.0
S	-	-	179	3428	3606	3366	5.3
Cl	-	11,300	-	-	11,300	8157	32.0
K	106	236	119	191	652	592	7.4
Ca	-	-	1421	-	1421	1533	6.4
Ti	5	-	22	-	27	31	32.2
V	3	-	-	-	3	7	39.3
Mn	2	2	6	-	10	12	24.2
Fe	91	-	331	-	422	529	8.7
Ni	1	-	-	-	1	3	29.3
Cu	-	-	8	12	20	22	23.2
Zn	19	-	27	1	47	55	17.5
As	-	-	8	-	8	8	76.3
Br	37	28	-	-	66	63	7.7
Rb	0	-	0	-	1	1	24.7
Sr	3	-	4	-	8	11	14.1
Zr	0	-	1	0	2	2	24.4
Mo	-	-	-	1	1	1	33.7
Pb	112	-	22	14	148	155	5.7
PM_{2.5}							
Mass	6.2	1.1	-	9.7	17.0	24.7	15.5
Mg	-	39	9	-	48	48	27.9
Al	-	-	14	-	14	29	51.3
Si	-	-	71	-	71	98	13.2
S	102	-	-	2876	2978	3017	19.9
Cl	-	120	-	-	120	119	38.2
K	-	-	-	149	149	142	21.1
Ca	-	-	90	-	90	104	13.8
V	2	-	-	-	2	6	39.3
Mn	0	-	2	-	2	5	39.0
Fe	19	-	41	4	64	69	28.0
Ni	0	-	-	-	0	2	71.8
Cu	-	-	0	2	3	5	28.0
Zn	6	-	6	7	19	23	20.5
As	-	-	-	8	8	5	38.9
Br	18	-	-	-	18	21	9.4
Rb	0	-	0	-	0	0	35.0
Ba	2	-	-	1	3	10	35.4
Pb	91	-	-	25	116	110	13.4

an important contributor to PM₁₀ (19.2 μg/m³) (see Table 2), its contribution was not statistically significant for PM_{2.5} (see Figures 3a and 3b). Considering the concentration of Si in this factor (119 ng/m³), the estimated soil contribution

should not exceed 0.4 μg/m³. A third factor, which was associated with sulfur, was resolved in both fractions (see Table 1). This source was attributed to transported emissions from distant sources. This factor was the exclusive contributor of sulfur and to a lesser extent of Pb, Cu, K, As, and Zn (see Table 2). The sulfur-related source contribution to both fractions was comparable—5.8 μg/m³ of PM₁₀ and 5.0 μg/m³ of PM_{2.5} (see Table 2; Figures 3a and 3b). Finally, K and Rb were highly associated with the fourth factor, which was attributed to wood combustion (see Table 2). Low amounts of Si, S, and Pb in the PM₁₀ fraction were associated with wood combustion; however, they were not resolved in the fine fraction. The contribution of emissions from wood burning was calculated at ~30% (10.3 μg/m³) and 15% (10.1 μg/m³) of the PM_{2.5} and PM₁₀ mass, respectively (see Table 2; Figures 3a and 3b).

Rancagua. Motor vehicle, wood burning, soil, and emissions from local Cu smelters and mechanical processing industries were resolved in both fractions in Rancagua. A large fraction of the total variance (98.0% for PM₁₀ and 94.2% for PM_{2.5}) was explained by these five factors. The entire PM_{2.5} mass concentration (calculated 43.0 μg/m³; measured 42.6 μg/m³) and the majority of PM₁₀ mass (calculated 70.8 μg/m³; measured 73.9 μg/m³) were accounted for by these sources (see Figures 2c and 2d). The first factor was attributed to automobile emissions. This source was an important source for Br and Pb. Also, a small fraction of K, V, Fe, Ni, As, Cu, Mo, and Zn was associated with this factor (see Table 3).

It is possible that emissions from the Cu smelter, which is another local source, are correlated with automobile emissions. Their estimated contribution was 5.9 μg/m³ for PM₁₀ and 8.5 μg/m³ for PM_{2.5} mass (see Table 3). Vehicle emissions were responsible for 7.9% of PM₁₀ and 18.7% of PM_{2.5}

(see Figures 3a and 3b). Furthermore, soil was the principle source (more than 90%) of the elements Al, Si, Fe, Ca, Ti, Sr, and Mg (see Table 3). In addition, a large fraction of K was present in PM_{10} . Overall, soil was an important source of PM_{10} ; it accounted for $23.7 \mu\text{g}/\text{m}^3$ (see Table 3), which represented 32% of the total PM_{10} mass (see Figures 3a and 3b). The regression coefficient of soil factor scores on $PM_{2.5}$ mass was not statistically significant; however, the expected soil contribution should be $\sim 3.0 \mu\text{g}/\text{m}^3$.

Because of the association of elements such as Ti, Cr, Mn, Fe, Zn, Zr, and Mo with one of the factors in both fractions, these factors were attributed to iron and steel industries (see Table 3). These industries operate within metropolitan Rancagua and support the major industrial operations of Cu smelters in this area. These elements were mostly associated with coarse particles (>40% of PM_{10} mass) (see Table 3). The contributions of this source to PM_{10} and $PM_{2.5}$ mass were ~ 6.0 and $3.3 \mu\text{g}/\text{m}^3$, respectively (see Table 3), which represented $\sim 8\%$ of both mass fractions (see Figures 3a and 3b). Wood and/or agricultural waste burning was also a major source of PM in Rancagua. Most of the K in the fine fraction and $\sim 32.6\%$ of the K in the PM_{10} fraction were associated with this source (see Table 3). Low amounts of Rb, Ca, Fe, and Br were also present in this factor, possibly because of the correlation between the contributions of wood burning, automobiles, and soil sources.

A large fraction of mass concentration in both fractions was associated with wood burning (47.3% for $PM_{2.5}$ and 27.5% for PM_{10}) (see Figures 3a and 3b). Indeed, wood combustion emissions contributed ~ 20.3 and $20.2 \mu\text{g}/\text{m}^3$ of the PM_{10} and $PM_{2.5}$ mass concentrations, respectively (see Table 3). Most of the concentrations of S, Cu, Zn, As, and Mo were explained by Cu smelter emissions (see Table 3).^{34,35} Sulfur emitted by the Cu smelters was mostly in the form of SO_2 .³⁴ Copper smelter emissions were responsible for almost 25% of PM_{10} and $PM_{2.5}$ mass. Indeed, they accounted for 14.9 and $11.0 \mu\text{g}/\text{m}^3$, respectively.

Viña del Mar. The FA results of the Viña del Mar PM_{10} and $PM_{2.5}$ mass and elemental data are shown in Table 4. Six and five factors were retained for PM_{10} and $PM_{2.5}$, which explained 99.09 and 98.27% of the total variance of the systems, respectively. As shown, the calculated and measured mass and elemental concentrations are in good agreement (see Figures 2e and 2f; Table 4). The calculated mass concentrations were slightly higher (PM_{10} : measured $55.5 \mu\text{g}/\text{m}^3$ vs. calculated $57.1 \mu\text{g}/\text{m}^3$; $PM_{2.5}$: measured $19.9 \mu\text{g}/\text{m}^3$ vs. calculated $21.8 \mu\text{g}/\text{m}^3$) (see Table 4).

The first source was the major contributor of Cu, As, Zn, Mo, and Pb concentrations, and it was attributed to the direct emissions from Cu smelters. As mentioned, a

separate factor source was resolved for sulfur. Smelter emissions were responsible for almost 2.8% ($1.5 \mu\text{g}/\text{m}^3$) of PM_{10} and 4.5% ($0.9 \mu\text{g}/\text{m}^3$) of $PM_{2.5}$ mass (see Figures 3a and 3b; Table 4). V and Ni concentrations were associated with the second factor, which was attributed to diesel emissions (from trucks or ships) and the local refinery. It is expected that sulfur is present in oil combustion or refinery emissions; however, sulfur was not associated with this source. A possible explanation is that this source contributed very little to the total sulfur; therefore, it was not possible to determine its contribution statistically. The contribution of oil combustion was minimal ($0.1 \mu\text{g}/\text{m}^3$ for PM_{10} and $0.2 \mu\text{g}/\text{m}^3$ for $PM_{2.5}$) (see Table 4), and it represented $\sim 1\%$ of the calculated PM_{10} and $PM_{2.5}$ mass (see Figures 3a and 3b).

Soil was identified as a source of PM in Viña del Mar. Most of the measured concentrations of crustal elements, Al, Si, Ca, Fe, and Ti, in both PM_{10} and $PM_{2.5}$ fractions were associated with this source (see Table 4). However, small fractions of other elements, such as Br, As, Cu, Zn, Pb, and K, were also associated with this factor in the PM_{10} fraction, possibly because of the resuspension of urban soil containing these elements. The contribution of soil to PM_{10} mass was $18.2 \mu\text{g}/\text{m}^3$ and represented 32.8%, while it was not statistically significant in the $PM_{2.5}$ fraction (see Table 4; Figures 3a and 3b). The fourth factor was associated with Br; thus, it was attributed to automobile emissions. This source was the exclusive source of Br (see Table 3). Furthermore, a large fraction of Pb was associated with motor vehicle emissions (see Table 4). Automobiles contributed $\sim 19.0 \mu\text{g}/\text{m}^3$ of the PM_{10} and $6.0 \mu\text{g}/\text{m}^3$ of the $PM_{2.5}$ (see Table 4). For both fractions, automobile emissions were responsible for $\sim 30\%$ (34.3% for PM_{10} and 30.0% for $PM_{2.5}$) (see Figures 3a and 3b).

Wood or agricultural waste burning was also an important source of both PM_{10} and $PM_{2.5}$. The majority of fine K was contributed by this source (see Table 4). In addition, comparable K concentration was associated with this factor in the PM_{10} fraction; the remainder was associated with soil particles. Small amounts of Fe, Rb, and Sr were also identified in this factor (see Table 4). The mass contribution of this source was $8.6 \mu\text{g}/\text{m}^3$ (15.5%) for PM_{10} and $5.6 \mu\text{g}/\text{m}^3$ (28.2%) for $PM_{2.5}$ (see Figures 3a and 3b; Table 4). A separate factor for sulfur was resolved. This source was responsible for the entire concentration of sulfur in both fractions (see Table 4). Furthermore, a small fraction of Cu, As, Zn, Pb, and to a lesser extent Ni and V, was associated with this factor (see Table 4). This suggested that the sulfur-related source was primarily correlated with emissions from Cu smelters. In addition, oil combustion was a minor source of sulfur in this area. The contribution of this source to PM_{10} and $PM_{2.5}$ was comparable ($8.4 \mu\text{g}/\text{m}^3$ for PM_{10} and $9.1 \mu\text{g}/\text{m}^3$ for $PM_{2.5}$) (see Table 4) and

accounted for ~15.1 and 45.9% of PM_{10} and $PM_{2.5}$, respectively (see Figures 3a and 3b). Finally, the contribution of sea salt particles was resolved only in the PM_{10} fraction. Chloride was associated exclusively with sea particles; however, the contribution of sea was minimal ($1.2 \mu\text{g}/\text{m}^3$) (see Table 4).

Valparaíso. Table 5 presents the results of the Valparaíso PM_{10} and $PM_{2.5}$ mass and elemental data. Seven factors were retained for PM_{10} and six for $PM_{2.5}$, which explained 97.8 and 99.2% of the total variance of the PM_{10} and $PM_{2.5}$ data sets, respectively. A comparison of the calculated and measured $PM_{2.5}$ is shown in Figures 2g and 2h, which also indicate that most of the variability in $PM_{2.5}$ is explained by the identified sources. The calculated PM_{10} and $PM_{2.5}$ mass concentrations were found to be ~24.3 and 15.4% less than the corresponding measured mass concentrations, respectively (see Table 5). This suggests that other sources, which were not identified by the FA, are also contributors to PM in Valparaíso.

As observed in Viña del Mar, which is located north of Valparaíso, two separate factors were resolved for Cu smelter emissions. Primary emissions of coarse and fine particles were associated with the first factor, which was an important contributor to Cu, Zn, and Mo (see Table 5). A considerable part of As in the fine fraction was also associated with this factor; however, trace amounts of As in the coarse fraction were identified in the corresponding factor (see Table 5). In addition, Pb was associated with this source, which agrees with the results from Rancagua (see Table 3) and Viña del Mar (see Table 4). Lastly, Cu smelter emissions accounted for 4.1 and $2.3 \mu\text{g}/\text{m}^3$ of the PM_{10} and $PM_{2.5}$ mass concentrations (see Table 5), which corresponded to 5.3 and 6.4%, respectively (see Figures 3a and 3b).

The second source was an important contributor to S and As for both PM_{10} and $PM_{2.5}$ (see Table 5). The atmospheric transformation of SO_2 , which is primarily emitted from Cu smelters, might be the reason for elevated S concentrations and their correlation to As. Thus, this source was attributed to distant smelter sources. This source contributed ~ $14 \mu\text{g}/\text{m}^3$ for both fractions ($14.0 \mu\text{g}/\text{m}^3$ for PM_{10} and $14.7 \mu\text{g}/\text{m}^3$ for $PM_{2.5}$) (see Table 5). Motor vehicles were the predominant source of Br and Pb in both fractions (see Table 5). Trace amounts of K, Ca, Sr, and Ba were also associated with this source. Motor vehicle emissions accounted for less than 13% ($5.0 \mu\text{g}/\text{m}^3$ for $PM_{2.5}$ mass and $7.3 \mu\text{g}/\text{m}^3$ for PM_{10}) for both fractions (see Figures 3a and 3b).

Diesel emissions from trucks or ships or from the local refinery were contributing to PM_{10} and $PM_{2.5}$ mass concentrations. This source was the major source of V and Ni (see Table 5). Sulfur was also identified in the oil

combustion or refinery emissions, which contributed ~1% of the measured PM_{10} ($0.3 \mu\text{g}/\text{m}^3$) and $PM_{2.5}$ ($0.4 \mu\text{g}/\text{m}^3$) (see Table 5). The contribution of this source is similar to that found in Viña del Mar (see Table 4). Wood burning was also a significant source of PM_{10} and $PM_{2.5}$ (10.9 and $8.1 \mu\text{g}/\text{m}^3$, respectively) (see Table 5). Comparable concentrations of K in the fine and PM_{10} fractions were identified in this source. In addition, traces of Ca, Br, and Rb were also identified in the PM_{10} fraction. The crustal elements (Si, Al, Ca, Fe, Ti, Mn, and Ba) were strongly associated with the sixth factor; thus, it was attributed to soil. As expected, soil was the major source of these elements in both fractions (see Table 5). The contribution of soil was ~ $21.0 \mu\text{g}/\text{m}^3$, which represented less than 30% of the measured PM_{10} (see Figures 3a and 3b). On the other hand, $0.1 \mu\text{g}/\text{m}^3$ of the $PM_{2.5}$ was explained by soil contribution. The contribution of sea salt particles was only resolved in the PM_{10} fraction. This source was the exclusive source of Cl, and it accounted for $1.2 \mu\text{g}/\text{m}^3$ (see Figures 3a and 3b; Table 5).

Iquique. The FA results of the Iquique PM_{10} and $PM_{2.5}$ mass and elemental data are shown in Table 6, and the calculated and measured mass and elemental concentrations are in very good agreement. Four factors were retained for the source apportionment analysis, which explained 96.8 and 93.2% of the total variance of PM_{10} and $PM_{2.5}$ systems. The first factor was associated with Br and Pb (see Table 6). However, other elements such as S and K were also present in this factor. Considering that the contributions of automobiles to $PM_{2.5}$ and PM_{10} are similar— 6.2 and $7.2 \mu\text{g}/\text{m}^3$, respectively—the estimates should be reasonable. Therefore, automobile emissions represented ~11% of PM_{10} and 25% of $PM_{2.5}$ in Iquique (see Figures 3a and 3b). Sea salt was the major source of Cl and Mg (see Table 6). This source represented a large fraction of PM_{10} ($23.8 \text{ mg}/\text{m}^3$), ~38%; however, it accounted for only $1.1 \mu\text{g}/\text{m}^3$ of the fine fraction (see Figures 3a and 3b).

Soil was the major source of the crustal elements Al, Si, Fe, Ca, and Ti (see Table 6), contributing $8.6 \mu\text{g}/\text{m}^3$, which represented almost 13% of PM_{10} (see Figures 3a and 3b). The regression of soil factor scores on $PM_{2.5}$ mass was not statistically significant. It is worth mentioning that the Ca/Si ratio is higher in Iquique than in the other cities. This is most likely due to the different soil composition in Iquique. The fourth factor was associated with sulfur, and it was attributed to the transport of emissions from local or distant smelters. The composition and strength of these emissions were comparable for both PM_{10} and $PM_{2.5}$ transported aerosol (see Table 6). A fraction of K, Pb, Zn, As, and Cu were each associated with this source. Local activities such as fish industries are the major sources of S and K. About 40% of both PM_{10} ($23.2 \mu\text{g}/\text{m}^3$) and

PM_{2.5} (9.7 µg/m³) was explained by this source (see Table 6; Figures 3a and 3b).

CONCLUSIONS

FA was applied to apportion the sources of aerosol in five major urban areas in Chile. The determined factors were rotated obliquely. Although this was not the only mathematically possible solution, the results obtained by this method for both mass and elemental data from the five cities were satisfactory. Using this method, we were able to separate collinear sources. The calculated daily scores of each factor were regressed on particle mass to estimate source contributions. The agreement between calculated and measured mass was good, and this was further supported by the relatively low %RMSE values. In addition, a satisfactory agreement between the source contribution on mass and elemental concentrations for both fractions was observed. The results were also consistent with known characteristics of source types associated with the factors.

Distinct differences in elemental concentrations were found among the different cities. This is not common in other countries. A mixture of both natural and anthropogenic sources were resolved for all five cities. Soil dust and sea were the predominant sources of coarse particles in the PM₁₀ fraction. Their contribution to the PM_{2.5} fraction was negligible. Anthropogenic activities, such as motor vehicles, wood burning, and industries, were responsible for the majority of fine particle mass. Motor vehicle and wood burning were significant sources of PM_{2.5} and PM₁₀ in almost all of the cities (wood burning was not identified in Iquique). Emissions from Cu smelters and oil refineries (and/or diesel combustion) were identified as sources of fine particles in the industrial cities of Rancagua and Valparaíso, and to a lesser extent in Viña del Mar.

ACKNOWLEDGMENTS

This study was supported by the Comisión Nacional del Medio Ambiente (CONAMA) and Cooperación Suiza al Desarrollo (COSUDE) of Chile. The authors would like to thank Maritza Jadrijevic Girardi and Yolanda Silva Cerna for their help in the coordination and interpretation of the results, and Rocío Toro Rodríguez, Luis Rodríguez Muñoz, Marcelo Corral Fuentes, Claudio Corvalán Robert, and Gustavo Farías Garrido for their assistance in the collection of samples.

REFERENCES

- Schwartz, J.; Morris, R. *Am. J. Epidemiol.* **1995**, *142*, 23-35.
- Schwartz, J.; Dockery, D.W.; Neas, L.M. *J. Air & Waste Manage. Assoc.* **1996**, *46*, 927-939.
- Pope, C.A.; Dockery, D.W. *Am. Rev. Respir. Dis.* **1992**, *145*, 1123-1128.
- Schwartz, J. *Environ. Res.* **1991**, *56*, 204-213.
- Pope, C.A.; Kanner, R.E. *Am. Rev. Respir. Dis.* **1993**, *147*, 1336-1340.
- Ostro, B.; Lipsett, M.J.; Mann, J.K.; Braxton-Owens, H.; White, M.C. *Inhal. Toxicol.* **1995**, *7*, 711-722.
- Ito, K.; Thurston, G.D. *J. Expos. Anal. Environ. Epidemiol.* **1996**, *6*, 79-95.
- Kelsall, J.E.; Samet, J.M.; Zeger, S.L.; Xu, J. *Am. J. Epidemiol.* **1997**, *146*, 750-762.
- Linn, W.S.; Gong, H., Jr.; Clark, K.W.; Anderson, K.R. *J. Air & Waste Manage. Assoc.* **1999**, *49*, 108-115.
- Chow, J.C.; Watson, J.G.; Fujita, E.M.; Lu, Z.Q.; Lawson, D.R.; Ashbaugh, L.L. *Atmos. Environ.* **1994**, *28*, 2061-2080.
- Koutrakis, P.; Wolfson, J.M.; Spengler, J.D. *Atmos. Environ.* **1988**, *22*, 157-162.
- Brauer, M.; Dumyahn, T.S.; Spengler, J.D.; Gutschmidt, K.; Hienrich, J.; Wichmann, H.E. *Environ. Health Perspect.* **1995**, *103*, 482-488.
- Van der Zee, S.C.; Hoek, G.; Harssema, H.; Brunekreef, B. *Atmos. Environ.* **1998**, *32*, 3717.
- Borja-Aburto, V.H.; Castillejos, M.; Gold, D.R.; Bierzwinski, S.; Loomis, D. *Environ. Health Perspect.* **1998**, *106*, 849-855.
- Ostro, B.; Sanchez, J.M.; Aranda, C.; Eskeland, G. *J. Expos. Anal. Environ. Epidemiol.* **1996**, *6*, 97-114.
- Ostro, B.; Chestnut, L.; Vichit-Vadakan, N.; Laixuthai, A. *J. Air & Waste Manage. Assoc.* **1999**, *49*, 100-107.
- Ilabaca, M.; Olaeta, I.; Campos, E.; Villaire, J.; Tellez-Rojo, M.M.; Romieu, I. *J. Air & Waste Manage. Assoc.* **1999**, *49*, 154-163.
- Rappengluck, B.; Oyola, P.; Olaeta, J.; Fabian, P. *J. Appl. Meteorol.* **2000**, *39*, 275-290.
- Artaxo, P.; Oyola, P.; Martinez, R. *Nucl. Instrum. Methods B* **1999**, *150*, 409-416.
- Kavouras, I.G.; Lawrence, J.; Koutrakis, P.; Stephanou, E.G.; Oyola, P. *Atmos. Environ.* **1999**, *33*, 4977-4986.
- Marple, V.A.; Rubow, K.L.; Turner, W.; Spengler, J.D. *J. Air Pollut. Control Assoc.* **1988**, *37*, 1303-1307.
- Houck, J.E.; Chow, J.C.; Watson, J.G. *Determination of Particle Size Distribution and Chemical Composition of Particulate Matter from Selected Source in California*; Prepared for the California Air Resources Board, Sacramento, CA, Contract No. A6-175-32, by Desert Research Institute: Reno, NV, 1989.
- Hopke, P.K.; Gladney, E.S.; Gordon, G.E.; Zoller, W.H.; Jones, A.G. *Atmos. Environ.* **1976**, *10*, 1015-1025.
- Henry, R.C.; Hidy, G.M. *Atmos. Environ.* **1979**, *13*, 1581-1596.
- Thurston, G.D.; Spengler, J.D. *Atmos. Environ.* **1985**, *22*, 9-25.
- Koutrakis, P.; Spengler, J.D. *Atmos. Environ.* **1987**, *21*, 1511-1517.
- Alpert, D.J.; Hopke, P.K. *Atmos. Environ.* **1980**, *14*, 1137-1146.
- European Commission. *Official Journal L* **1999**, *163*, Annex I and III.
- National Ambient Air Quality Standards for Particulate Matter: Proposed Decision. *Code of Federal Regulations*, Part 50, Title 40; *Fed. Regist.* **1996**, *61*, 65638-65713.
- Brook, J.R.; Dann, T.F.; Burnett, R.T. *J. Air & Waste Manage. Assoc.* **1997**, *47*, 2-19.
- Parkhurst, W.J.; Tanner, R.L.; Weatherford, F.P.; Valente, R.J.; Meagher, J.F. *J. Air & Waste Manage. Assoc.* **1999**, *49*, 1060-1067.
- Allen, G.; Sioutas, C.; Koutrakis, P.; Reiss, R.; Lurmann, F.W.; Roberts, P.T. *J. Air & Waste Manage. Assoc.* **1997**, *47*, 682-689.
- Babich, P.; Wang, P.-Y.; Allen, G.; Sioutas, C.; Koutrakis, P. *Aerosol Sci. Technol.* **2000**, *32*, 309-324.
- Romokroger, C.M.; Llona, F. *Atmos. Environ.* **1993**, *27*, 401-404.
- Romokroger, C.M.; Morales, J.R.; Dinator, M.I.; Llona, F.; Eaton, L.C. *Atmos. Environ.* **1994**, *28*, 705-711.
- Kavouras, I.G.; Mihalopoulos, N.; Stephanou, E.G. *Nature* **1998**, *395*, 683-686.

About the Authors

Ilias G. Kavouras (corresponding author; e-mail: kavouras@hsph.harvard.edu) is a research associate and Petros Koutrakis is a professor of environmental sciences at the Harvard School of Public Health, Boston, MA. Francisco Cereceda-Balic is an associate professor of atmospheric sciences at Universidad Técnica Federico Santa María, Valparaíso, Chile. Pedro Oyola is a senior advisor of the Comisión Nacional del Medio Ambiente, Region Metropolitana, Santiago de Chile, Chile.