

Elemental Composition of Airborne Particulate Matter from Santiago City, Chile, 1976

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In Chile, the State Public Health Office (Ministerio de Salud Pública) is responsible for pollution control and for air quality. This office has been monitoring only toxic gases and total suspended particulate matter.^{1,2}

The present work is the first study in Chile designed to determine trace elements and their concentrations in particulate matter in the air. By use of enrichment factors, 25 trace elements are classified according to natural or anthropogenic origin.

Experimental Procedure

There were two sampling periods: July (winter) and September (spring), 1976. Four sites were studied, located about 6 km north, south, west and east of downtown Santiago (Table I). The south, north and west sites are urban and 500 m above sea level. The east site is suburban and approximately 270 m higher than the others.

Twenty-four-hour samples were collected on Whatman-41 cellulose filter paper, in a modified stainless steel

Buchner funnel.³ Approximately 10 m³ were used at the urban sites and 200 m³ at the suburban site.

Instrumental neutron activation analysis (INAA) was used as the analytical technique. In using this technique, special attention must be given to the preparation of reference samples; they must be as chemically and physically alike as possible. Therefore, in this work, the reference samples were prepared by settling measured volumes of solutions of eighteen elements on Whatman-41 filter paper; the references for the other seven elements (Se, Sb, Sc, Eu, Gd, Hf, and Th) were prepared using Andesite AGV-1 reference samples from the U.S. Geological Survey. Corrections were made to allow for physical and chemical differences between both references.

When the samples and references were prepared using Whatman-41, the filter paper was always folded and pelletized (3 ton/cm²). In this way we could reproduce the counting and irradiation geometry and use all the filter paper, eliminating the error generated by a nonhomogeneous distribution of particulate matter. The irradiations were

made at the RECH-1 nuclear reactor of the Chilean Commission of Nuclear Energy.

For the determination of Na, Mg, Al, Cl, Ca, V, Mn, and Cu, samples were first irradiated for 10–30 s, at a neutron flux of 2×10^{13} n/cm² × s, and counted after irradiation by a Ge (Li) detector joined to a 4096 multichannel Hewlett-Packard analyzer. A second 8-hour irradiation followed, with a neutron flux of 6.5×10^{12} n/cm² × s; counts were taken 4 days later for As, Br, and La determinations and 30 days later for Sc, Cr, Fe, Co, Zn, Se, Rb, Sb, Cs, Ce, Eu, Gd, Hf, and Th determinations, using the detector mentioned above.

The areas of the peaks were integrated using the Covell method and the total area method.⁴ The quantities of the different elements were calculated by the comparator method.⁴ The detection limit, D.L., was calculated according to Currie,⁵ considering that the elements of the sample had concentrations similar to the mean values obtained.

The mean percent error of each determination was calculated considering the number of peaks used to calculate the quantity of the element. If only one

peak was considered, the propagated error of a quotient (% E), was calculated. If the radionuclide had several peaks, the error was calculated as a standard deviation (% E').⁶

Table II shows the mean percent error obtained for the two seasons studied and the D.L. of the 25 trace elements analyzed.

Results and Discussion

In Santiago a substantial part of the high pollution levels found can be attributed to meteorological and topographical factors. Low wind speed, the high number of stillness periods, and temperature inversions cause a stable atmosphere and slow pollutant dispersion.⁷ On the other hand, the valley is almost completely surrounded by mountains with heights ranging from 3500–4000 m on the east to 1000–2000 m on the north, west, and south.

In order to analyze results independent of meteorological conditions, enrichment factors (E.F.) were used.^{8,9} These factors take into account the relative enrichment of the elements as compared to their relative abundances in local rocks and soil. In this way, if the E.F. of an element is greater than one, the element can be assigned an anthropogenic origin; if E.F. equals approximately one, it can be assigned a natural origin.

For this method, only the relative concentrations are considered, and the concentrations of the elements in the earth crust are assumed to be exactly known. Mason's values¹⁰ were used as a first approximation.

Table III shows the mean E.F. for the samples taken in the urban sites and in the suburban site in the two periods. The normalizing element is Sc.

The E.F. values range from 0.5 (Na) to 2370 (Sb); these results are normal where natural or anthropogenic origins are expected.

Santiago is about 130 km from the Pacific Ocean, and separated from it by the coastal mountain range. Under these circumstances it seemed of interest to determine the existence of a relative sea salt contribution to the urban atmospheric aerosols. To do this we followed Rahn¹¹ in order to consider the enrichment factor plots of the studied element and the concentration ratios versus Al. We analyzed Na, Mg, Ca, Cs, Cl, Cu, Zn and Br. In these conditions, Santiago can be classified as a non-marine city.

We have found that the following elements with E.F. > 6 can be assigned an anthropogenic origin: Cl, Cu, Zn, As, Se, Br, and Sb. On the other hand, Na, Mg, Al, Ca, Sc, Fe, Rb, La, Ce, Eu, Gd, Hf, and Th can be assigned a natural origin (E.F. < 2). There is a third group of elements, V, Cr, Mn, Co and Cs (2 < E.F. < 6) for which assignment is not clear.

Table I. Date, number and volume of air samples taken in Santiago, Chile, 1976.

Site	Winter 1976			Spring 1976		
	Date (July)	No. of samples	Volume (m ³)	Date (Sept.)	No. of samples	Volume (m ³)
North	4–10	12	13	20–27	14	10
South	13–20	12	14	20–27	14	12
West	26–30	5	12	12–16	4	12
East	27–31	4	180	22–28	6	230

Table II. Mean percent error (% E or % E')^a and detection limits (D.L.) for the elements analyzed in winter and spring.

Elements	Winter		Spring		D. L. $\mu\text{g} \times 10^3$
	% E	% E'	% E	% E'	
Na		5.6		4.4	1363
Mg	31.8		25.0		12425
Al	1.9		6.9		31
Cl		2.8		6.3	721
Ca	8.2		18.4		4332
Sc		6.8		6.1	1.3
V	4.2		5.2		26
Cr	3.9		5.5		64
Mn		3.4		4.0	47
Fe	3.4		3.1		5100
Co		4.5		2.5	7.2
Cu	24.2		28.3		288
Zn		9.5		10.1	324
As		13.7		14.6	0.14
Se		28.9		37.7	1.6
Br		3.7		7.1	2.1
Rb	49.2		47.9		162
Sb		11.8		10.5	9.8
Cs	17.8		25.3		12.0
La		6.3		16.1	1.1
Ce	11.1		13.8		17.0
Eu		25.7		27.3	0.44
Gd	29.0		26.1		5.1
Hf		22.1		26.5	3.7
Th		18.8		21.3	2.4

^a % E = mean percentual error for radionuclides with one peak. % E' = mean percent error for radionuclides with several peaks.

Table III. Mean enrichment factors for the urban sites and suburban site in the two periods sampled in Santiago. Normalizing element: Sc.

Element	Mean enrichment factors			
	Winter		Spring	
	Urban	Suburban	Urban	Suburban
Na	1.1	0.5	0.9	0.7
Mg	5.4	0.8	1.5	1.2
Al	1.1	1.3	1.2	1.7
Cl	322.0	85.0	122.0	234.0
Ca	2.5	1.9	2.1	1.7
V	6.7	3.4	4.3	6.0
Cr	23.0	0.8	13.0	1.0
Mn	3.5	2.0	2.4	2.2
Fe	1.6	1.0	1.2	1.0
Co	3.3	1.3	5.6	1.4
Cu	38.0	11.0	27.0	31.0
Zn	159.0	44.0	48.0	47.0
As	60.0	38.0	26.0	26.0
Se	213.0	14.0	433.0	21.0
Br	288.0	88.0	122.0	96.0
Rb	5.1	0.6	1.0	0.7
Sb	767.0	249.0	380.0	2370.0
Cs	6.6	2.7	4.2	3.0
La	2.3	1.0	1.4	0.9
Ce	2.4	1.5	1.9	1.4
Eu	2.0	1.4	1.6	1.6
Gd	2.5	1.6	2.3	1.3
Hf	1.9	2.7	1.7	0.9
Th	1.4	0.6	1.0	0.9

Thus, the same elements with large E.F. values reported elsewhere were found to be anthropogenic. Our values are smaller than Neustadter *et al.*⁹ due to the presence in Santiago of only one coal-fired power plant (Zn, As, Sb, Cl), and the existence of only a small number of Al smelting works (Cl). Br is probably emitted from gasoline motor vehicles.

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In Chile, the Superintendencia de Salud (NCS) (Ministry of Health and Public) is responsible for environmental and for air quality. The latter has been collaborating with the U.S. EPA and other international organizations.

The present work is the first study in Chile aimed at determining trace elements and their concentrations in particulate matter in the air. By use of analytical techniques, 25 trace elements were determined according to natural or anthropogenic origin.

Experimental Procedure

Three sites were selected previously and designated as "background" (Fig. 1). The first sites were selected, located along the coast, with good ventilation characteristics (Tables I, II). The second sites, and were sites with high traffic volume and were sites with a commercial and manufacturing zone in their vicinity (Fig. 1). The third sites were selected with low traffic volume and were sites with a commercial and manufacturing zone in their vicinity (Fig. 1).

Each filter holder¹ approximately 10 cm² was used at the background sites and 200 cm² at the urban sites.

Instrumental neutron activation analysis (INAA) was used as the analytical technique. In using this technique, special attention must be given to the preparation of reference samples, that must be as chemically and physically as far as possible. Therefore, in this work, the reference samples were prepared by weighing measured volumes of crystals of various elements on Whatman 41 filter paper. The differences in the filter paper elements (Se, Sb, Sn, Mo, Cd, Bi, and Pb) were prepared using Analytical Reagent reference samples from the Geological Survey, Columbia.

When the samples and standards were prepared, Whatman 41, the filter paper was pre-baked and pre-ashed in a muffle furnace at 450°C for 24 hours. The samples and standards were pre-ashed in a muffle furnace at 450°C for 24 hours. The samples and standards were pre-ashed in a muffle furnace at 450°C for 24 hours.

Each of the filter holder was placed in the Chilean Commission of Nuclear Energy.

For the determination of Se, Sb, Sn, Mo, Cd, Bi, and Pb, samples were fast irradiated in the INAA standard flux of 10¹⁴ neutrons/cm² and counted after irradiation in a Ge(Li) detector coupled to a W.P. Spectroscopic System. The detector was a silicon drift detector (SDI) with a resolution of 1.5 keV. The detector was calibrated with a series of standard sources.

The gross count rates were corrected for decay and self-absorption. The concentration of the elements in the air was calculated by the comparison with the standard count rates. The detection limit was calculated by the Currie formula.

The data were analyzed by using the method of least squares. The results are presented in Tables I, II, and III.