

Total element concentration and chemical fractionation in airborne particulate matter from Santiago, Chile

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Abstract

Total element determination and chemical fractionation were carried out in airborne particulate matter (PM₁₀) from the Cerrillos monitoring station in Santiago, Chile, sampled in July (winter), 1997–2003.

Element concentration in the period under study (1997–2003) was statistically analyzed through cluster analysis in order to identify groups of elements having similar behavior along time. Elements such as Cd, Cu, Pb, Ni, As and Mg show a clear decrease in concentration with time. On the contrary, chromium increases its concentration almost linearly during the period.

In order to estimate whether the presence of a certain element in PM₁₀ matrix is mainly due to anthropogenic or natural processes, the enrichment factor of each element was determined.

According to their behavior in the sequential extraction procedure, the elements were grouped by multivariate analysis in three clusters: (a) those mobile elements (Pb, Cd, Zn, Mn, Cu and As) which are weakly bound to the matrix (fractions 1 and 2) (b) those elements (V, Ti, and Cr) mainly bound to carbonates and oxides (fraction 3) and (c) the most immobile elements (Ni, Mo, Ca, Mg, Ba and Al), mainly bound to silicates and organic matter (fraction 4). A source of great concern is the fact that elements of such high toxicity as Pb, Cd and As are highly concentrated in both mobile fractions, indicating that these elements have a direct impact on the environment and on the health of the exposed population.

Keywords: Total element concentration; Chemical fractionation; PM₁₀; Santiago–Chile

1. Introduction

In Chile, nearly 90% of the population lives in urban areas. The rapid economic growth of the country has brought with it adverse effects on air quality. This situation affects mainly Santiago city, which concentrates about 40% of the total Chilean population. These factors together with geographi-

cal location and meteorological conditions of poor ventilation make the Santiago population exposed, every day, to high levels of atmospheric pollution by particulate matter coming mainly from anthropogenic sources.

The city of Santiago is surrounded by mountain ranges and in winter, air flow inside the basin is much weaker than in summer as a result of the smaller availability of solar radiation, giving rise to continuous thermal inversion episodes.

The plan of prevention and atmospheric decontamination of Santiago city involves a number of

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instruments that allow facing and solving the existing environmental problems, among them the daily measurement and collection of airborne particulate matter (particle size $\leq 10 \mu\text{m}$, PM_{10}).

The effect of particulate matter on the population depends on its size and composition. Particle size determines the degree of penetration and permanency of these particles inside the respiratory system. Fine particles settle in the pulmonary alveoli, affecting them directly. Once deposited in the respiratory system, their action depends on their chemical composition and toxicity.

The organic compounds that form particulate matter, especially polycyclic aromatic hydrocarbons (PAHs), are potential carcinogens because their metabolites are highly reactive and form covalent bonds with proteins and genetic material (DNA and RNA), thus giving rise to carcinogenic and mutagenic processes. Regarding the inorganic composition of atmospheric aerosols, most trace elements contained in PM_{10} are also potential carcinogens, especially in the respiratory tract. Lead is particularly important because it is caught by some epithelial cells of the alveoli, causing morphological alterations in them.

On the other hand, the determination of total metal content in airborne particulate matter samples is a poor indicator of metal bioavailability, mobility and toxicity, because these properties depend on the chemical association of the trace elements with the different components of the solid matrix. In this context, a chemical fractionation process provides an additional level of information because it allows to classify trace elements according to their solubility in specific reagents, which can be associated to bonding to some specific matrix component. Fractionation of trace elements in airborne particulate matter would indicate their mobility once the particles are mixed directly in natural waters during scavenging of the aerosols by wet deposition or after particles are inhaled by human beings.

Different studies have been done regarding metal fractionation of atmospheric aerosols applying sequential chemical extraction. According to a recent review (Smichowski et al., 2005), the sequential chemical fractionation schemes over the last 15 years can be classified into five main categories: (1) based on Tessier's procedure (Tessier et al., 1979), (2) based on Chester's procedure (Chester et al., 1989), (3) based on Zatká's procedure (Zatká et al., 1992), (4) based on BCR procedure (Ure et al., 1993) and (5) other procedures.

In this study we use a four-stage fractionation method based on Chester's procedure. A first extraction step with water was included to this fractionation in order to establish the distribution of metals among water soluble, environmentally mobile, bound to carbonates and oxides and environmentally immobile (bound to organic matter and silicates) fractions. Fernández et al. (2002) suggest the previous use of water because these conditions are more similar to lung condition. Airborne particulate matter (PM_{10}) collected at Cerrillos monitoring station (Metropolitan Region of Chile) during July (years 1997–2003) was analyzed. As far as we know, the present study is the first one related to element fractionation in PM_{10} in Chile.

2. Experimental

2.1. Reagents

All chemicals used were of analytical-reagent grade. Deionized water (Nanopure ultrapure water system; Barnstead, Dubuque, Iowa, USA) was used throughout.

The ICP multielement standard was obtained from High Purity Standards (QCS-26).

2.2. Sampling

Quartz fiber PM_{10} filters provided by the Metropolitan Environmental Health Service (SESMA) of Santiago, Chile, were analyzed. The filters analyzed correspond to those used daily at Cerrillos monitoring station (south-west of Santiago city) in July 1997–2003 (most extreme winter season). One-half of each daily (24 h period) sampled filter was analyzed by the Metropolitan Environmental Health Service. The other halves were preserved and recently provided to us. In the present application, we integrated a 1-month sample. All the PM_{10} filters collected in July of each year (1997–2003) were separately grouped by weeks. One circular part of each filter, equivalent to an area of 1.53 cm^2 , was cut by using a hole-puncher of 14 mm diameter and extracted sequentially according to the procedure established in Table 1. The extracts obtained for each week were composed to obtain a sample extract representative of the month.

The selected scheme was based on Chester's procedure (Chester et al., 1989), in which a first step of extraction with water was included. The conditions are given in Table 1.

Table 1
Fractions, reagents and conditions in the sequential extraction procedure

Fractions	Reagents	Operating conditions
Water soluble	10 ml deionized water	15 min constant agitation (room temperature), 15 min centrifugation (3000 rpm). The supernatant is preserved with drops of nitric acid pH < 2 at 4 °C. The residue is weighed before starting the following step
Environmentally mobile	25 ml of 1 mol l ⁻¹ CH ₃ COONH ₄ (pH 7) solution	15 min constant agitation (room temperature), 15 min centrifugation (3000 rpm). The supernatant is preserved with drops of nitric acid pH < 2 at 4 °C. The residue is weighed before starting the following step
Bound to carbonates and oxides	25 ml of (1 mol l ⁻¹ NH ₂ OH · HCl + 25% (v/v) CH ₃ COOH) mixture	6 h constant agitation (room temperature), 15 min centrifugation (3000 rpm). The supernatant is preserved with drops of nitric acid pH < 2 at 4 °C. The residue is weighed before starting the following step
Organic and refractory-associated	10 ml of HNO ₃ + 2 ml of HF, 1 ml of H ₂ O ₂	Microwave oven digestion, evaporation in hot plate, dilution to 25 ml. Kept at 4 °C until analysis

2.3. Determination of element concentrations in the extracts

After the extraction process, 14 analytes were determined directly by ICP-MS (Fisons VG-PlasmaQuad) in each fraction. The values obtained in $\mu\text{g L}^{-1}$ were expressed in $\mu\text{g m}^{-3}$ considering volume of air sampled ($1627\text{ m}^3\text{ day}^{-1}$), area of each impacted PM₁₀ filter (513 cm^2), filter area used in the analysis (1.53 cm^2) and number of sampling days (filters) in July of each year (not < 25).

2.4. Determination of enrichment factor (EF)

EFs were calculated by using the following equation:

$$EF = \frac{([E]/[Al])_{PM_{10}}}{([E]/[Al])_{crust}}$$

where $([E]/[Al])$ corresponds to concentration ratio between the element, E, and aluminum as reference in the aerosol (PM₁₀) and the earth crust, respectively.

2.5. Statistical analysis

Multivariate analysis of the data was carried out through cluster analysis using the Ward's method and Euclidean distances.

3. Results and discussion

Total concentrations of the elements present in PM₁₀ at Cerrillos monitoring station in Santiago (July, years 1997–2003) are shown in Table 2.

The concentrations found in this study were calculated as the sum of the four fractions obtained in the sequential extraction procedure. By way of comparison, total concentrations were also obtained in some samples through acid digestion (US-EPA, 1994), which was carried out just like the last stage of the sequential extraction procedure. However, results show that in all instances total concentrations obtained through acid digestion were approximately 30% lower than those obtained through the sum of the four fractions. Likewise, previously reported total concentrations in the same PM₁₀ filter samples (years 1997–2000), treated either with acidified subcritical water (Morales-Riffo and Richter, 2004) or by acid digestion (SESMA, 2002), were lower than concentrations reported here. It is known from previous studies (Falciani et al., 2000) that analytical methods for sample preparation using microwaves, such as US EPA 3051, do not provide total digestion for many sample matrices. In this context, Hassan et al. (2007) have recently carried out the modification of a number of parameters for microwave digestion, resulting in significant improvement in recoveries for many elements in different matrices, including airborne particulate matter.

A comparison between the element concentrations found in this study in Cerrillos and those measured in other districts of Santiago city in wintertime, 1998 (Artaxo, 1998) and in the atmosphere of Chillan, Chile (Celis et al., 2004), showed that for most elements, concentrations in PM₁₀ from Cerrillos are inside the reported ranges, except for Ni, V and Cr which are from two to three times higher in Cerrillos. This is consequent with industrial activity of the district.

Table 2
Total concentration of elements ($\mu\text{g m}^{-3}$) in PM_{10} in the period 1997–2003

Elements	Year						
	1997	1998	1999	2000	2001	2002	2003
Al	2.99	3.82	3.63	2.62	2.71	2.82	2.62
Mg	1.51	3.94	2.59	1.30	1.39	1.34	1.43
Ca	7.81	11.23	9.22	6.09	6.18	7.97	6.43
Zn	0.93	0.86	0.64	0.71	0.62	1.08	0.45
V	0.93	0.97	0.80	0.59	0.41	0.65	0.42
Pb	0.96	0.83	0.49	0.20	0.10	0.10	0.08
Ti	0.97	0.98	0.86	0.72	0.69	0.75	0.68
Mo	0.06	0.05	0.09	0.07	0.04	0.04	0.04
Ni	0.06	0.03	0.02	0.02	0.02	0.02	0.02
As	0.19	0.18	0.21	0.05	0.05	0.04	0.05
Mn	0.10	0.11	0.08	0.08	0.06	0.08	0.06
Cr	0.24	0.33	0.48	0.51	0.57	0.82	0.92
Cu	0.32	0.30	0.20	0.15	0.09	0.08	0.09
Ba	0.47	0.37	0.78	0.39	0.41	0.18	0.38
$\text{Cd}/10^{-2}$	0.50	0.63	0.41	0.27	0.23	0.25	0.21

Mean of three independent determinations. Relative standard deviation (RSD) was always $<5\%$.

Element concentration in the period under study (1997–2003) was statistically analyzed through cluster analysis in order to identify groups of elements showing similar behavior along time. The dendrogram, which is a tree for visual classification of similarity and is shown in Fig. 1, indicates that multivariate analysis allowed the identification of four clusters.

Elements such as Cd, Cu, Pb, Ni, As and Mg show similar behavior concerning their attenuation in concentrations over the period. In all cases it is possible to see (Table 2) a clear decrease in concentration with time, which seems highly consistent with the implementation of the decontamination plan applied in central Chile since 1998. Particularly outstanding is the considerable attenuation of lead concentration due to the gradual elimination of leaded gasoline in Chile. The decreasing concentrations of copper and arsenic should be related to the enforcement of air quality standards and subsequent implementation of pollution abatement plans and emission reduction schedules mainly by state-owned copper concentrate smelters. Reduction of nickel and cadmium concentrations can be related to the reduction of particulate matter emitted by industries located in the vicinity of the Cerrillos monitoring station and also to the decrease in the use of coke as a fuel. Concentrations of cadmium in airborne particulate

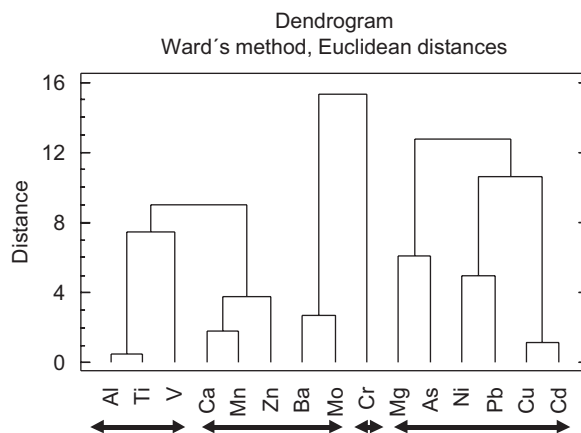


Fig. 1. Dendrogram obtained in cluster analysis for total concentration of elements in PM_{10} from Cerillos monitoring station in years 1997–2003.

matter have been reported (Fergusson and Ryan, 1984) in the interval from 1 to 300 ng m^{-3} , depending on the location and nature of the pollution source. Fortunately, this study shows that in Santiago the concentration of Cd in all cases is very low ($<6 \text{ ng m}^{-3}$).

On the other hand, Al, Ti and V showed similar concentrations during the period, decreasing slightly from 2000. This effect can be associated to minimization of powder suspension by the application of street cleaning programs involved in the decontamination plan of Santiago city.

The elements Ca, Mn, Zn, Ba and Mo, show a net diminution in their concentrations during the period but without a clear trend. The net reduction in concentration for all this group of elements is mainly because the concentration of PM_{10} as a whole has been reduced in this period (Morales-Riffo and Richter, 2004).

Contrary to the behavior of the other elements, chromium increased (Table 2) its concentration almost linearly during the 1997–2003 period. Considering that Cerrillos monitoring station is located in a district with considerably high industrial activity, it is highly probable that the increase in Cr concentration resulted from the increase in local industries of metal treatment like chrome plating or smelters.

In order to estimate whether the presence of a certain element in PM_{10} matrix is mainly due to anthropogenic or to natural processes, the EF of each element was determined (Table 3).

According to the high EF observed for elements such as Mo, As, Cr, Zn, Cd, Pb, V, Cu and Ni, it is

possible to establish that these elements are generally emitted by anthropogenic sources. The EF for all these elements, except for Cr, decreases in the period under study, which confirms, especially for Pb, As and Cu, the effectiveness of the decontamination plan applied in the country during the last years. Elements such as Ba, Ca, Ti, Mn and Mg, instead, showed low EF and, for most of them, this value is relatively constant, which suggests a natural emission source. Taking into account some data available in the literature regarding element concentrations in Chilean soils (Carrasco and Préndez, 1991), EF was also calculated (values in parentheses, Table 3) for some elements. It may be more representative to use these values rather than earth crust concentrations. As can be seen in Table 3, EF decreased significantly for Pb, Cu and Cd, considering the high content of these elements in Chilean soils. However, the EFs are still high enough to consider an anthropogenic origin. Instead, EF increased for Cr and Ni, emphasizing the anthropogenic character of their presence in PM₁₀.

3.1. Distribution of the elements in the different fractions of the sequential extraction

Fractionation data (Table 4) for the elements in the different years are shown as percentage of the sum of concentrations found in the four steps of the sequential extraction procedure.

According to the results, the elements were grouped by cluster analysis (Fig. 2) depending on the fraction(s) to which the respective element is associated. Three groups were identified by this multivariate analysis: (a) those mobile elements (Pb, Cd, Zn, Mn, Cu and As) which are weakly bound to the matrix (fractions 1 and 2) (b) those elements (V, Ti and Cr) mainly bound to carbonates and oxides (fraction 3) and (c) the most immobile elements (Ni, Mo, Ca, Mg, Ba and Al), mainly bound to silicates and organic matter (fraction 4).

The mobility order of elements in PM₁₀ is shown in Fig. 3. A cause of great concern is the fact that elements of such high toxicity as Pb, Cd and As are highly concentrated in both mobile fractions, which indicates that these elements have a direct impact on the environment and on the health of the exposed population.

Fig. 4 shows the distribution of lead in the four fractions. It can be seen that the sum of the first two mobile fractions for this element fall in the interval 94–70%, constituting a high source of environmental pollution in the receiving media. However, it is also possible to observe that the water soluble fraction decreased in the period 1997–2003 (from 68% to 18%), suggesting a change in the main source of lead pollution as a result of the decline in the use of leaded gasoline. It is important to mention that leaded gasoline was allowed in Chile until March 2001. Regarding Pb behavior in PM₁₀,

Table 3
Enrichment factor from PM₁₀ in the period 1997–2003

Element	Year						
	1997	1998	1999	2000	2001	2002	2003
Pb	2108 (397)	1428 (269)	890 (168)	502 (94)	235 (44)	229 (43)	199 (37)
As	1339	2177	2670	920	777	597	805
Mo	1074	764	1347	1385	771	768	841
Cd	687 (33)	680 (32)	468 (22)	429 (20)	351 (17)	363 (17)	328 (16)
Zn	367 (200)	264 (144)	207 (113)	319 (174)	269 (147)	452 (247)	201 (110)
Cr	66 (119)	71 (129)	109 (198)	159 (290)	173 (315)	240 (438)	291 (530)
V	190	155	134	138	93	140	98
Cu	160 (58)	117 (42)	82 (30)	86 (31)	51 (18)	45 (16)	50 (18)
Ba	31	19	41	29	29	13	28
Ca	5	6	5	5	5	6	5
Ti	5	4	3	4	4	4	4
Mn	3 (3)	3 (2)	2 (2)	3 (2)	2 (2)	2 (2)	2 (2)
Mg	2	4	3	2	2	2	2
Ni	24 (62)	10 (26)	7 (18)	10 (25)	6 (16)	9 (24)	8 (22)
Al	1	1	1	1	1	1	1

Values in parentheses correspond to the EF calculated considering concentrations of the elements in continental Chilean soils (Carrasco and Préndez, 1991) instead of earth crust.

Table 4
Percentages obtained from the elements in each fraction of the sequential extraction procedure in the period 1997–2003

Element	Year	Fractions				Element	Year	Fractions				Element	Year	Fractions			
		1	2	3	4			1	2	3	4			1	2	3	4
Pb	1997	68.2	25.5	4.5	1.7	Cr	1997	3.3	15.0	78.2	3.5	Ba	1997	17.4	6.7	21.3	54.7
	1998	62.1	29.9	6.0	2.0		1998	2.9	9.7	82.7	4.7		1998	14.9	10.6	15.7	58.8
	1999	50.7	38.8	6.9	3.6		1999	0.9	8.2	89.3	1.6		1999	9.5	13.3	16.4	60.8
	2000	38.9	46.5	9.3	5.3		2000	0.6	5.7	92.0	1.6		2000	17.5	7.0	2.1	73.5
	2001	37.9	27.0	28.3	6.8		2001	0.8	25.7	72.3	1.2		2001	12.8	3.4	13.8	69.9
	2002	27.1	41.7	24.0	7.3		2002	0.9	4.4	93.4	1.2		2002	12.8	3.4	13.8	69.9
	2003	18.2	52.3	21.5	8.0		2003	0.4	4.5	94.1	1.0		2003	15.2	6.7	13.4	64.7
As	1997	60.3	9.8	21.4	8.5	Ti	1997	3.9	ND	92.7	3.3	Ca	1997	39.3	9.0	10.1	41.7
	1998	62.2	16.7	13.4	7.7		1998	3.7	ND	93.4	2.9		1998	36.7	8.0	10.7	44.7
	1999	64.2	17.4	11.5	6.9		1999	ND	ND	97.4	2.6		1999	29.9	6.1	7.7	56.3
	2000	57.0	19.3	10.9	12.8		2000	ND	ND	97.6	2.4		2000	31.7	5.9	16.7	45.7
	2001	42.5	0.0	57.5	ND		2001	1.8	24.9	71.1	2.2		2001	24.0	9.6	15.0	51.5
	2002	54.7	22.4	23.0	ND		2002	5.6	ND	90.9	3.5		2002	29.7	7.1	14.4	48.7
	2003	48.4	15.3	36.3	ND		2003	ND	ND	95.8	4.2		2003	31.3	8.7	8.0	52.0
Cu	1997	61.7	3.9	8.1	26.3	V	1997	5.4	ND	93.9	0.7	Al	1997	7.7	ND	7.5	84.8
	1998	71.1	5.7	10.9	12.4		1998	3.2	ND	96.8	ND		1998	6.3	ND	5.7	88.0
	1999	44.8	2.8	10.4	42.0		1999	ND	ND	100.0	ND		1999	5.0	ND	5.4	89.6
	2000	37.4	2.5	11.0	49.1		2000	ND	ND	100.0	ND		2000	4.3	ND	1.7	94.0
	2001	59.1	5.8	9.9	25.2		2001	3.0	26.6	70.4	ND		2001	2.6	1.6	1.4	94.4
	2002	52.6	ND	15.3	32.2		2002	4.7	ND	95.3	ND		2002	3.2	ND	2.2	94.7
	2003	57.2	ND	17.4	25.4		2003	ND	ND	97.7	2.3		2003	1.6	ND	2.1	96.4
Zn	1997	84.1	10.4	3.1	2.4	Ni	1997	32.3	ND	11.4	56.3	Mg	1997	18.6	2.7	6.8	71.8
	1998	80.8	8.2	3.4	7.6		1998	34.8	ND	25.4	39.8		1998	7.9	26.6	25.1	40.5
	1999	57.0	6.4	ND	36.6		1999	24.0	ND	20.5	55.6		1999	10.0	12.0	28.6	49.4
	2000	70.3	4.1	7.9	17.8		2000	ND	ND	38.2	61.8		2000	14.1	1.5	5.0	79.5
	2001	74.4	2.1	3.4	20.1		2001	25.3	ND	29.6	45.1		2001	10.1	3.1	4.8	82.0
	2002	44.7	5.0	1.8	48.5		2002	33.7	ND	35.8	30.5		2002	15.3	5.1	4.6	75.1
	2003	76.7	10.6	ND	12.8		2003	27.9	ND	24.9	47.1		2003	8.9	2.0	4.8	84.2
Mn	1997	71.2	3.9	10.4	14.5	Mo	1997	47.0	11.7	5.3	36.0	Cd	1997	90.5	3.9	ND	5.6
	1998	68.6	4.4	10.0	17.0		1998	25.4	9.1	4.6	60.9		1998	83.9	7.4	3.9	4.8
	1999	60.6	4.5	10.1	24.9		1999	44.5	12.6	6.3	36.7		1999	79.2	7.3	4.2	9.4
	2000	66.9	4.8	7.8	20.4		2000	53.3	10.2	4.3	32.3		2000	91.0	9.1	ND	ND
	2001	59.2	6.1	8.4	26.3		2001	24.0	6.7	6.1	63.3		2001	75.8	7.7	7.1	9.5
	2002	63.8	5.4	10.5	20.3		2002	16.2	7.8	ND	75.9		2002	78.3	11.7	ND	10.1
	2003	56.0	5.6	13.7	24.8		2003	30.1	13.8	ND	56.1		2003	83.6	16.4	ND	ND

Mean of three independent determinations. Relative standard deviation (RSD) was always <5%. 1: Water soluble; 2: environmentally mobile; 3: bound to carbonates and oxides; 4: organic and refractory-associated. ND, not detected.

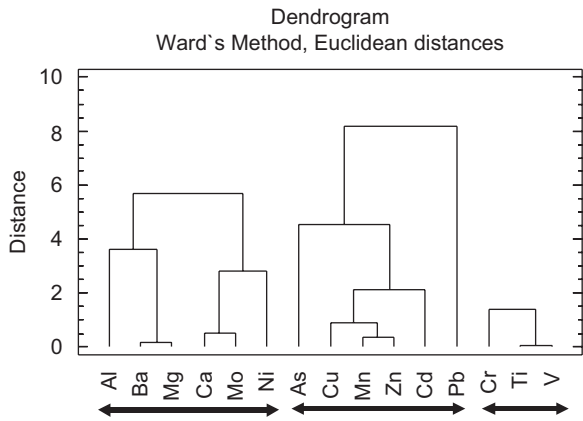


Fig. 2. Dendrogram obtained in cluster analysis for fractionation of 14 elements.

different results have been reported depending on the location of the source and particle size. A high mobility of lead (40%) was observed previously in Hungary (Bikkés et al., 2001). The authors carried out a fractionation of elements considering both chemical bonding and particle size and observed that Pb presented a unimodal distribution at a maximum of $<1\ \mu\text{m}$, indicating that the anthropogenic source of this element is traffic. On the contrary, in Seville, Spain (Fernández et al., 2002) Pb was found mainly bound to carbonates and oxides (33.2%) and to the organic matter, oxidizable and sulphidic fractions (35.3%) when $<0.61\text{-}\mu\text{m}$ particles were analyzed. The mobile fraction in these particles was only 3.8%.

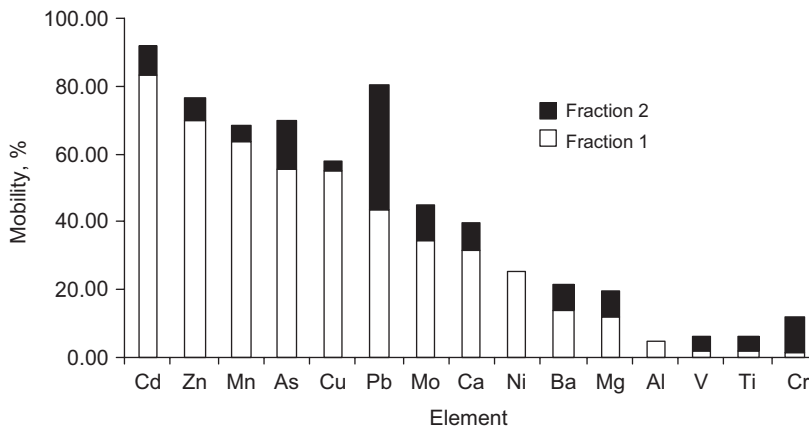


Fig. 3. Average mobility of the element in the period under study (1997–2003). Mobility is expressed as the percentage of element concentration extracted in fractions 1 and 2.

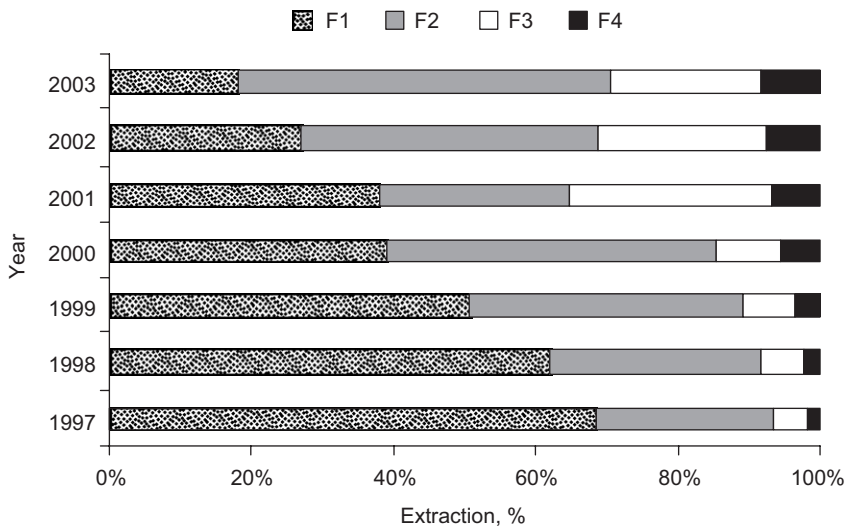


Fig. 4. Distribution of lead in the different fractions of the sequential extraction procedure.

The authors established that the main emission source would also be vehicular traffic. According to our results, it is evident that when the emission source is mainly traffic (period 1997–1999), the resulting compounds of lead in PM₁₀ are highly water soluble, which decreases concomitantly with the reduction of this source.

Arsenic, like lead, is basically distributed in the most mobile fractions (near 70%), not appearing or appearing near 10% (years 1997–2000) bound to the organic matter and silicate fraction. In Hungary (Veszprém city, and region of Kabhegy) (Hlavay et al., 1996), instead, arsenic was found mainly distributed in the immobile fraction (percentages from 88% to 94%), and only from 3% to 10% in the environmentally mobile fraction. This indicates that probably the emission source in those places is significantly different from the ones in Chile. Emissions of arsenic from copper smelters are primarily in the form of reduced oxide, As₂O₃, which can be solubilized in aqueous media as H₃AsO₃. On the other hand, it is highly probable that the arsenic extracted from the third fraction (bound to carbonate and oxides) corresponds to As(V), because the anionic species HAsO₄²⁻ would be strongly retained by positively charged iron and aluminum oxides.

The high mobility observed in the case of Cd (Fig. 3) has also been previously described. For example, Harrison et al. (1981) studied the chemical associations of cadmium and other trace elements in street dust and they concluded that Cd may have a significant component that is readily available. Similarly, just as in this study, it was reported (Hlavay et al., 1996) that in urban aerosol, cadmium is almost completely in the exchangeable form, which is considered mobile.

Distributions of Cu, Zn and Mn are very similar; these elements appeared mostly in the mobile fraction (water soluble), reaching average values of 55%, 70% and 64% of the total element, respectively. However, their relative presence in the stable fraction (organic matter and silicate fraction) is also important, showing average percentages of 30%, 21% and 21%, respectively. Such phenomena can be explained as a combination of anthropogenic and natural processes. On the other hand, association between Cu and Mn could be attributed to incineration (Chow, 1995; Fernández et al., 2002).

The second group identified in cluster analysis corresponds to those elements mainly bound to carbonate and oxides. For Cr, V and Ti, the

percentage of this fraction was over 80%. Similarly, in particulate matter collected in Seville, Spain, Cr is mainly bound to this fraction but to a lower extent (40%) than in the present case (Fernández et al., 2000). In <0.6- μ m particles from Seville (Fernández et al., 2002), Ti was bound to carbonates and oxides in a large percentage of 43.6%, but this element was mainly bound to the immobile fraction in 45.2%. In the same study, V was associated in 25.1% to the carbonate and oxide fraction and it was mainly leached in the soluble and exchangeable fractions in 50.4%. Even though the fraction associated to carbonate and oxides is of less environmental mobility, relative to the first two fractions, the toxicity associated to these elements would be equally high considering that this fraction is bioavailable through the lung (Fernández et al., 2002).

The third identified group corresponds to elements in which the immobile-associated fraction is the most important. In this group we find Ni, Mo, Ca, Mg, Ba and Al. Of these elements, aluminum appears by far as the most immobile element, near 92% being associated to the organic matter or silicate fraction (aluminosilicates). However, in the case of Ni, Mo and Ca, the water soluble fraction is also important (approximately 30–40%).

In previous studies, Ni has also been found mainly associated to immobile fractions (Fernández et al., 2000, 2002; Hlavay et al., 1996). In Seville (Fernández et al., 2000, 2002), this metal has been associated to an important extent to the organic matter or sulphidic fractions. The authors state that metals associated to organic matter pass easily through lung tissues, and therefore Ni could cause toxicity. In Hungary (Hlavay et al., 1996), in the polluted city of Veszprém and in a background place (Kabhegy), Ni was mainly bound to the immobile fraction of particulate matter in 57% and 65%, respectively. As in our observations, Ni was also found near 20% in the mobile fraction.

Calcium presents a low EF (Table 3); consequently, its presence in PM₁₀ is mainly associated to the soils. This is consistent with the fact that calcium in soils is highly concentrated, probably as CaCO₃ or associated to clay minerals (Alloway, 1990).

The case with molybdenum is different because it is mainly introduced to the atmosphere by anthropogenic sources (associated to copper mining activity and steel industry). The immobile fraction corresponds approximately to 50% and the sum of the first two mobile fractions is approximately 40%

in average. It has been reported (Spectrum Laboratories Inc., 2003) that in ambient air in urban areas, molybdenum ranged from 0.01 to 0.03 $\mu\text{g m}^{-3}$, corresponding to lower values than the ones observed in this study at Cerrillos (Table 2).

4. Conclusions

The total element content and chemical fractionation in airborne particulate matter (PM_{10}) from the Cerrillos monitoring station in Santiago de Chile were studied. The samples for analysis were taken in July (winter), 1997–2003.

Regarding total concentration of elements, multivariate analysis allowed the identification of four clusters. It is possible to see a clear decrease in concentration of Cd, Cu, Pb, Ni, As and Mg along time, which seems highly consistent with the implementation of the decontamination plan applied in central Chile since 1998. The considerable attenuation of lead concentration due to the gradual elimination of leaded gasoline in Chile is remarkable. On the other hand, Al, Ti and V showed similar concentrations during the period, decreasing slightly from year 2000 onwards. The elements Ca, Mn, Zn, Ba and Mo, show a net diminution in their concentrations during the period but with no clear trend. On the contrary, chromium increased its concentration almost linearly during the period 1997–2003, probably due to the increase in the local industries of metal treatment.

Taking the EFs into account, it was possible to establish that Mo, As, Cr, Zn, Cd, Pb, V, Cu and Ni, are generally emitted by anthropogenic sources. Elements such as Ba, Ca, Ti, Mn and Mg, instead, showed low EF and, for most of them, this value is relatively constant, which suggests a natural emission source.

On the other hand, three groups were identified by this multivariate analysis when the sequential extraction procedure was applied to the samples: (a) mobile elements: Pb, Cd, Zn, Mn, Cu and As (fractions 1 and 2), (b) elements mainly bound to carbonates and oxides: V, Ti and Cr (fraction 3) and (c) immobile elements mainly bound to silicates and organic matter: Ni, Mo, Ca, Mg, Ba and Al (fraction 4). The fact that elements of such high toxicity as Pb, Cd and As are highly concentrated in both mobile fractions, which indicates that these elements have a direct impact on the environment and on the health of the exposed population is a source of great concern.

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