A chemical speciation of trace metals for fine urban particles

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Abstract

The chemical speciation of 11 metals in aerosols has been studied in 12 areas of the city of Seville (Spain). Urban particles were collected with a high-volume sampling system equipped with a cascade impactor, which effectively separates the particulate matter into six size ranges. Forty-one samples were collected in the spring of 1996. The chemical speciation was studied in the finest particles of the impactor system (<0.61 μm), those that can penetrate into the alveolar region of the lung. This speciation scheme is specific for urban particles and consisted of four fractions: 1. soluble and exchangeable metals; 2. carbonates, oxides and reducible metals; 3. bound to organic matter, oxidisable and sulphidic metals; 4. residual metals. The sample extractions were analysed for 11 metals by inductively coupled plasma atomic emission spectrometry (ICP-AES). The chemical speciation of metals showed that the metals with highest percentages in the different fractions are vanadium (50.4%) in the soluble and exchangeable fraction, calcium (39.7%) in the carbonates, oxides and reducible fraction, magnesium (59.2%) in the bound to organic matter, oxidisable and sulphidic fraction, and iron (54.6%) in the residual fraction. Correlations between all the variables have been studied and the results showed common sources to the metal fractions correlated in relation to the industrial activities and mainly the vehicular traffic.

Keywords: Chemical speciation; Speciation scheme; Trace metals; Air pollution; Urban particles; Fine particles; Inductively coupled plasma atomic emission spectrometry

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1. Introduction

Urban populations are exposed to metals in suspended particles, and these are often well above natural background levels owing to anthropogenic processes. When this fact results in elevated metal concentrations, it can pose serious risk to human health. Metals contained in suspended particulate matter are considered to be a health hazard since they can be absorbed into human lung tissues during breathing. For this reason, a great deal of research has focused on the metal composition of atmospheric suspended particulate matter. However, determination of metal levels is usually limited to estimating the quantity of total suspended particles (TSPs), PM_{10} or $PM_{2.5}$ particles. Although these measurements can give some indication of the general pollution level in an area, they provide information neither on the size distribution nor on the chemical speciation of the metals. There is growing recognition that particulate standards based on TSP or PM_{10} alone are insufficient (EPA, 1999). The degree of respiratory penetration and retention is a direct

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function of the aerodynamic particle size. Particles <1-2 μm in aerodynamic diameter (a.e.d.) are predominantly deposited in the alveolar regions of the lung where the adsorption efficiency for trace elements is 60-80% (Infante and Acosta, 1991) and can affect lung physiology, especially if the particles contain biologically available toxic metals. Besides the study of the size distribution of metals carried out in Seville (Fernández et al., 2001), in which some toxic metals were accumulated in the smallest particles, it is also necessary to know the distribution of their chemical forms in these small particles with the aim of knowing the toxicity.

It is often necessary to quantify specific metallic forms since bioavailability, solubility, geochemical transport and metal cycles largely depend on physical-chemical speciation. Knowledge of the chemical speciation of the particles is vital in understanding the effects on human health.

Therefore, the objective of this study is to attain a knowledge of the chemical speciation of metals in fine particles in a typical city, influenced mainly by vehicular traffic, also by the resuspended land particles and some industrial focuses. Because the study of the chemical distribution of the toxic metals is of great interest for the health of the population of large cities, 11 metals were studied by chemical speciation. Seven of these metals had already been analysed with a Tessier's derived scheme not specific for urban particles in 1993 (Table 1) at the same sites in Seville (Fernández et al., 2000). In this present work, the chemical speciation in the fine urban particles is determined with a new speciation scheme optimised in 1996 in a doctoral thesis (Table 2). In our previous study (Fernández, 1998), the first objective of the optimisation was to know what experimental conditions of the speciation scheme were the most suitable for urban particles, since the majority of speciation schemes had been applied to sediments. The second objective was to extract the chemical forms from particles that can be biologically available to the respiratory tract of the human body. Therefore, the experimental conditions of the scheme were determined in search of similar conditions of deposition and solubilisation into the lung. These resulting conditions were different from the Tessier's derived scheme. Therefore, when the experimental conditions of the 1993 and 1996 schemes were applied on the same samples, the concentrations of the chemical forms in the speciation fractions were different in many metals. These changes are due to the employment of less aggressive conditions in the new scheme of 1996. Furthermore, these conditions were more similar to the lung condition. In brief, the main differences of the new scheme can be summarised as follows:

(1) Water is used instead of sodium chloride. The soluble metallic species (chlorides, sulphates, nitrates, acetates, etc.) can be extracted and the exchangeable metallic species can also be extracted at the same time by the ionic strength of the first dissolved metallic species of the particles. Also, sodium metallic species of the particles can be measured in the extraction samples, although quartz or membrane filters would be needed.

(2) The concentration of the hydroxylamine chloride is different. Acetic acid is not used to acidify. The temperature of the extraction is the environmental one. High temperatures are not used, therefore causing the extraction of the bioavailable chemical forms to be more truthful.

(3) pH and concentration of the ammonium acetate are different. Nitric acid is not used. These experimental conditions are less aggressive, thus leaving this fraction extract only bound to organic matter, oxidisable and sulphidic chemical forms and not part of the residual metals.

(4) The more important differences are in the first two fractions, therefore, the expected important changes in their percentages will affect the percentages of the last two fractions.

2. Experimental part

2.1. Measurement sites

The physical and chemical speciation of metals in suspended particles has been studied in a network of 12 sampling stations in the city of Seville (37°23'N and 5°58'W) in Andalucia, Spain. The 12 selected sampling stations show different traffic intensities and also represent some industrial areas of Seville, as well as sites with cleaner air. This selection took into account the World Health Organisation (WHO-WMO, 1977) and the Environmental Protection Agency (EPA, 1975) recommendations. The network is designed to distribute the sites to cover practically the whole urban area and some zones of interest on the periphery of Seville. The main sources of contamination in Seville had been previously studied in 1985-1986, and the complete description of each sampling site had been made in our previous works (Usero et al., 1988; Fernández et al., 1999). All of these areas are densely populated. Approximately 25% of the automobiles in Seville are diesel fuelled, and the rest use gasoline. Lead is associated with traffic in Seville. This study was conducted in 1996-1997, but it was only after 1991 that cars were manufactured exclusively with catalysers, therefore, causing all the pre-1991 cars still using leaded fuel and the automotive population in 1996 to still be considered old.

2.2. Particulate sampling

Atmospheric particulate matter was collected with a high-volume sampling system (MCV, Model CAV-A/HF) equipped with a five-stage standard cascade impactor (MCV, Model IC/CAV) (Fernández et al., 2001) with a backup filter. Suspended particulates enter the impactor at a flow rate of 68 m^3 h^{-1} through the parallel slots in the first impactor stage. Particles larger than the particle cut-off size of the first stage impact on the slotted collection filter. The air stream then passes through the slots in the collection paper, accelerates through smaller slots in the second impactor stage, and the remaining particles greater than the particle cut-off size of the second-stage impact on the second collection filter…and so on. The impactor effectively separates the particulate matter in six stages with the following equivalent cut-off diameters, at 50 % efficiency: >10, 10-4.9, 4.9-2.7, 2.7-1.3, 1.3-0.61 and <0.61 μm (0.61-0.01) (Backup). For stages 1-5, five cut fibreglass filters were used (14.2 x 14.2 cm^2), and for the backup filter, a complete non-cut filter (20.3 x 25.4 cm^2) was used, i.e., a set of six filters for each sampling. Cut and non-cut fibreglass filters were purchased from WHATMAN (GF/A).

Granulometric fractions used here are in accordance with the American Conference of Governmental Industrial Hygienists (ACGIH, 1994) which defines the respirable fraction as having a median cut-off point at 4 μm a.e.d. Therefore, particles over 4 μm are classified as coarse particles, those between 1 and 4 μm are medium, and those under 1 μm are designated as fine particles (ISO 7708, 1995).

Care was taken in handling the fibreglass filters in order to avoid contamination problems and all filter materials and samples were handled within a vertical laminar airflow cabinet, thereby ensuring air cleanliness standards of class 100 according to Federal Standard 209E (FED-STD-209E, 1988).

Forty-one samples were collected in the spring of 1996 (April-June). A weekly sample was usually taken on different days over the following weeks, so that a possible distorting effect could be avoided. The sampling periods were 24-72 h (9-9 a.m. and air volumes 1700-4900 m^3). After sampling, all filters were stored at under 5% relative humidity (R.H.) at room temperature and in darkness.

In the previous work, the whole filters from stages 1 to 5 and a fourth of the filter from stage 6 were used to determine the metal size distribution for each sample. In the current work, another fourth of each filter from stage 6 of the same set of samples has been used to determine the chemical speciation of metals. Therefore, all speciation data of this present work are for the size fraction <0.61 μm a.e.d. of the particulate matter.

2.3. Reagents and apparatus

The vertical laminar airflow cabinet was from INDELAB with a HEPA filter (Model IDL-48V). Water bath was from JULABO (Model SW-20C). Centrifuge was from SIGMA (Model 3-15). Nitric, hydrochloric and perchloric acids, hydroxylamine chloride, ammonium acetate and hydrogen peroxide, and standard solutions for metals were from MERCK. Milli-Q-grade water was from WATERS-MILLIPORE (Model Plus).

The sample extractions were analysed in four chemical fractions for 11 elements (Mg, Ca, Ti, V, Mn, Fe, Co, Ni, Cu, Cd, and Pb) by inductively coupled plasma atomic emission spectrometry (ICP-AES) using a Fisons-ARL 3410 sequential multielement instrument provided with a data acquisition and control system IBM PC. The standard operational conditions of this instrument are summarised as follow: the carrier gas, coolant gas and plasma gas is argon at 80 psi of pressure, the carrier gas flow rate is 0.8 l min^{-1}, the coolant gas flow rate is 7.5 l.m^{-1}, the plasma gas flow rate is 0.8 l min^{-1} and the integration time is 1 s. One mini-torch consumes argon gas at a radio frequency power of 650 W. Consequently, it is capable of consuming a few millilitres of sample at a flow rate of 2.3 ml min^{-1} to measure the 11 metals. This fact allows the concentration of the extraction samples at 15 ml and this way the metals usually measured by GFAAS in our previous works (Cd, Co, Ni and Mn) in 50-ml standard flasks can also be measured by ICP-AES. A total of 41 x 4 = 164 particle size fractions were analysed for 11 elements representing 1804 individual different concentration measurements which were done in triplicate. The reported results are averaged values. Although attempts were made to measure sodium, aluminium, potassium, zinc, chromium and barium concentrations, these could not be accurately determined due to the high levels of these elements in the fibreglass filters used. To accurately measure these interesting elements, quartz filters would be needed.

2.4. Methodology for the chemical analysis

The filters used for dust collection were previously dried in a desiccator under 5% R.H. for a 48- h period and then weighed to a precision of ±0.1 mg on an analytical balance at 50% R.H. The humidity of the dark room was controlled to 50% with a heating-cooling system. After collection, used filters were placed in the desiccator, dried for another 48-h period and weighed again at 50% R.H. The suspended particulate matter concentration was then determined by dividing the mass by the air volume.

Chemical speciation of the metals was determined by applying the sequential extraction scheme shown in Table 2. The sequential procedure was as follows: the experimental conditions of the soluble and exchangeable fraction were applied to a fourth of a backup filter. Then the experimental conditions of the carbonates, oxides and reducible fraction were applied to the residue of the backup filter treated with the previous fraction, and so on until the fourth fraction. Chemical speciation was carried out in polypropylene centrifugal tubes by adding a fourth of a backup filter and subsequently applying the corresponding experimental conditions. Fifteen millilitres of each reagent was consistently added to the tubes. Extractions were carried out in a rotator at ambient temperature. Centrifugation was performed at 5000 rpm for 10 min. Having completed the extraction and centrifugation, the tube was left to decant by pouring the liquid into other conical tubes of 15 ml, which were then measured by ICP-AES.

The matrix effect due to the particle and filter matrix was studied through the standard addition technique in the four speciation fractions. The standard addition verified that this matrix effect was null. Regarding the interference matrix due to the reagents, the calibration curves have been obtained with the same matrix as each one of the four speciation fractions.

Since individual blanks were not available for each filter used for sampling, a set of unexposed backup filters was analysed using the same procedure used for actual samples. The mean

unexposed filter value was subtracted from each sample to obtain the best estimate of each element in the particulate matter.

2.5. Statistical analyses

The obtained results of the analytic measurements are in the form of 11 x 4 = 44 speciation fractions and 41 particle samples. There are many fractions and some of these can possibly be related to each other. To relate many variables, the analysis of correlations has been used in all previous works. The statistical correlations have then been studied by applying the CSS:STATISTICA (StatSoft) software package. The interpretation of the correlation results consists in assigning a common source to the metal fractions correlated, in relation to the main sources of this city, such as the traffic, the land particles and the industrial activities. In our case, when the chemical forms of one metal increase their concentration in the air, parallel to other chemical forms of another metal through different sampling sites and different days, we consider that these chemical forms of these metals come from the same emission source. Because of this, a data matrix (41 x 44) was obtained. Because a high correlation coefficient does not necessarily imply linearity, linearity was verified by graphical examination. Any non-linear case was discarded. The procedure for this not only consisted in choosing the highest correlation coefficients, but rather the linearity was also verified observing the linear profile of the points, i.e., the pairs of data x-y. Sometimes, high correlation coefficients do not give a real linearity on graph because their line is formed by an accumulation of points in an extreme of their linear range and a lone point at the other extreme. In theses cases, the correlation coefficients are due only to one sample and not due to all the experimental data. They are misleading and should therefore be discarded.

3. Results and discussion

The impactor stage fractionation of particles showed typical bimodal distributions (Fernández et al., 2001), one corresponding to a mode below 1.3 μm (55 %), and the other to a mode around 10 μm (32%). The finest particles, those below 0.61 μm, represent over 50% of the total particles (TSP). The 11 metal concentrations were determined in the previous work, and their chemical form concentrations have been determined in this current work. Therefore, not only the total concentration and toxicity but also the potential bioavailability of these species is now known.

The chemical speciation of the metals in the fine particles and the concentrations in ng m^{-3} of each chemical form are shown in Table 3. The range of minimum and maximum concentrations is also shown. The table also contains the sum of the four fractions that represents the total metal concentration in the fine particles. This table gives an indication of how much of each metal is speciated in each fraction. If this is compared with the guidelines for trace metals in airborne particles, such as the World Health Organisation guidelines (WHO, 2000) or the European guidelines (EC, 2000), even the sum of the four chemical forms does not reach its guideline value in almost all the cases. For example, the WHO guideline values are 1000 ng m^{-3} for vanadium, 500 ng m^{-3} for lead, 150 ng m^{-3} for manganese and 5 ng m^{-3} for cadmium, while the sums of the averaged concentrations of the four speciation fractions are 4.08, 43.7, 7.43 and 0.21 ng m^{-3}. However, the WHO nickel unit risk for lung cancer is 0.38 ng m^{-3}, while the average of the soluble and exchangeable chemical forms and the oxidisable chemical forms concentrations are 0.57 and 0.40 ng_m^{-3}, respectively. The WHO considered this metal as a carcinogenic air pollutant, which exceeds this risk limit in most bioavailable chemical forms. Regarding the European Commission guideline, the values are 500 ng m^{-3} for lead, 5 ng m^{-3} for cadmium and 10-50 ng m^{-3} for nickel.

All the experimental concentrations of the chemical forms, even the total sum concentrations, do not reach these values. However, the limit value based on cancer, unit risk approach are 0.24-0.55 ng m^{-3} for cadmium and 2.6-4.0 ng m^{-3} for nickel, while the sums of the averaged concentrations of the four speciation fractions are 0.21 ng m^{-3} for cadmium and 1.44 ng m^{-3} for nickel. These experimental values are very close to the unit risk values, although it should be kept in mind that these experimental concentrations correspond to particles <0.61 μm. Thus, the concentrations corresponding to the PM$_{10}$ or PM$_{2.5}$ particles will be greater than these unit risk concentrations. Therefore, this city has a polluted environment, and the health implications are very serious. Moreover, some chemical form concentrations, such as all those of nickel and the fraction bound to organic matter or sulphidic and the residual of cadmium, exceed the WHO and the EC unit risks.

In general, the chemical speciation obtained for the metals followed a similar distribution to that observed previously in 1993 but with some different percentages. This similar distribution may indicate the same composition of the sources. Multivariate statistical analyses were used to demonstrate that the composition of sources in Seville were the same from 1985 until 1993 (Fernández et al., 1999). It could be interesting to repeat this statistical method with these new speciation concentrations for corroboration if the sources found in 1993 are also the same until 1996. This aim could constitute the issue of another wide research. Regarding the different percentages in Table 4, these represent the changes resulting from the good optimisation of the 1996 scheme for urban particles. Lead is the metal that has changed most, and it is fortunate that Pb was found in less-bioaccesible fractions, since it is the heavy and toxic metal most abundant in the urban air of a large city, as seen in Table 3. This is because if the experimental conditions of the 1993 scheme were used, the conclusions about the bioavailability of the metals would be inexact, whereas when using the experimental conditions of the 1996 scheme, these conclusions are near reality, thanks to the improvement of the method. The new experimental conditions of the two first fractions in the 1996 scheme are less aggressive than those of the 1993 scheme; therefore, it is expected that the percentages of several metals in these fractions decrease in comparison with the 1993 results.

In Fig. 1 the concentrations in percentages of the 11 metals in the respective speciation fractions can be seen graphically. The chemical speciation shows important differences between the different metals. One group of metals is present in high percentages in the soluble and exchangeable fraction, the most easily available to human body through breathing. These are vanadium (50.4%), nickel (39.9%), cobalt (35.1%) and manganese (32.5%). The metals that have higher percentages in the carbonates, oxides and reducible fraction, and are also bioavailable through the lung, form a second group. These metals are calcium (39.7%), lead (33.2%) and cobalt (27.9%). These first two fractions are the most bioavailable and contain toxic metals. The metals that have higher percentages in the bound to organic matter, oxidisable and sulphidic fractions form a third group. These metals are magnesium (59.2%), titanium (43.6%) and copper (42.7%), but also lead (35.3%), manganese (33.8%), calcium (32.1%), cadmium (30.9%) and nickel (28.1%). And the non-bioavailable metals, like iron (54.6%) and titanium (45.2%) form the last group.

In the 1993-1994 work, the percentage distribution of the species agreed quite well with those obtained in Barcelona in 1985 (Fernández et al., 2000) using the same scheme in both (Obiols et al., 1986). In the present work, a modified speciation scheme was used, and these percentages are, in some metals, different from the percentages obtained in our 1993-1994 work, as shown in Table 4. This difference is expected since our new speciation scheme determines the metal chemical forms, which can enter the human body through the respiratory tract, as explained above. This change notably affects some metals like cadmium, manganese, cobalt, nickel and especially lead in the soluble and exchangeable fraction. It also affects the metals iron, lead, cadmium and mainly copper in the reducible fraction. Lead and cadmium have lower percentages in the soluble and

exchangeable chemical forms in the 1996 scheme. Manganese and cobalt have softer decreases in this fraction. However, nickel chemical species increases its percentage in the soluble fraction. In the carbonates, oxides and reducible fraction, the metals copper and iron have lower percentages, while the decrease of the lead percentage is softer. In this fraction, the cadmium chemical form increases its percentage. In the bound to organic matter, oxidisable or sulphidic fraction, the metal chemical forms greatly increase their percentages, such as the cadmium, iron and manganese species. The metals lead and copper have softer increases, and the metals nickel and cobalt have softer decreases. In the residual fraction, only the nickel species increases its percentage softly, while the lead, cobalt and copper species have higher percentages than in the 1993 scheme, like the iron chemical forms. In brief, the decreases in the bioavailable fractions are encouraging because cadmium and lead, objects of study by the EC, are very toxic. However, the same is not expected for nickel because of the increase in the soluble fraction.

Regarding the statistical correlations, the table of coefficients is formed by 41 x 44 = 1804 numbers. Because there are many fractions, the correlation coefficients have been considered starting from 0.75, and 10 correlations ≥ 0.75 have been found. A two-tailed t-test was done with a 95% confidence level for assessing if $r \neq 0$ significantly, and it has been so for all the correlated fractions above 0.75. These ten principal correlations are shown in Table 5. The metal chemical fractions have been indicated in the 'M(f.n)' form, when 'M' is the metal and n is the number of the speciation fraction. It can be observed that seven of the ten coefficients correspond to correlations between metals bound to organic matter or sulphidic metal. Practically, all the metal implicated usually appears associated to traffic exhausts and industrial activities (Fernández et al., 1999, 2000). Therefore, because Seville has little industrial activity, 4.1% of the total economic activities (Junta de Andalucía, 1987-2000; Ayuntamiento de Sevilla, 1993-1999), the main source of continuous anthropogenic particles and organic carbon in this city is vehicular traffic, although it is not as abundant as the natural source of the land particles. This fact is well known by our local and regional government and through an official statement by the European directives some time ago. The metals most correlated are Pb and Cu, as in our 1993 sampling campaign, where this association came from the traffic. In addition, Pb and Cu are also associated with the metal Cd, as in 1993. In addition, the correlations of the manganese with the copper in the fractions 1, 3 and 4, with the calcium in the fractions 1 and 3, and with the magnesium in the fraction 3 are numerous. If one considers the wide bibliography on chemicals from particles in different emissions sources (Chow, 1995), we could attribute the combinations of Mn with Cu and Ca could be attributed to the motor vehicle or vegetative burning (Mn, Ca) and to incineration (Mn, Cu). These possible sources lead one to think that these metals can come from the very frequent waste incineration in our city. The other pair of metals correlated is V with Ni. In this case, the typical metals that are usually components of the combustion of coal or oil fuels form the last correlations in the organic or sulphidic fraction. Regarding the nickel compounds, they are most likely sulphidic compounds (EC, 2000).

4. Conclusions

Eleven metals, seven of which had been analysed with a speciation scheme not specific for urban particles in 1993 at the same sites in Seville, were studied in 1996-1997 with a new improved speciation scheme.

In the study of size distribution of these samples, the particles under 0.61 μm represented over 50% of the total aerosol, and the metals that predominated in these particles were the toxic metals vanadium, nickel, lead and cadmium (Fernández et al., 2001). In the present work, we concluded that, additionally, nickel and especially vanadium and nickel compounds of Seville are very soluble. These particles can reach the lungs and remain there if the body does not provide a

mechanism for their elimination. These properties of solubility have recently been kept in mind by the European Commission in their working group on As, Cd and Ni compounds for the proposal for the 4th Daughter Directive under the Air Quality Framework Directive 96/62/EC (EC, 2000). In this document, nickel compounds of natural origin are likely to be silicate-oxidic in nature and then insoluble in water. However, nickel compounds from anthropogenic sources, mainly emitted by combustion, are predominantly soluble species such as nickel sulphate with lesser amounts of oxidic nickel and complex nickel oxides, whereas industrial processes may also emit metallic nickel and nickel alloys. Also, Ni and V are correlated in the chemical fraction of metal bound to organic matter or sulphidic metal. These metals have a strong relationship with the combustion of fuels used in the industrial activities of the city. Other metals are also correlated in this fraction, such as Pb with Cu and Cd. In this case, these metals have a relationship with the combustion of fuels used in vehicular traffic. These statistical results increase the knowledge of the metal sources in the air that were already studied in the previous work (Fernández et al., 2000).

In summary, the application of this new speciation scheme has made it possible to isolate the chemical forms in particulate matter that are really harmful for toxicological study, while leaving total metal contents as a pollution indicator.

Acknowledgments

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Table 1
Speciation scheme according to Obiols (1986)

Metallic fraction	Reagent	Experimental conditions
1. Soluble and exchangeable metals	25 mL of 1% NaCl	Mechanical agitation during 60 min at room temperature
2. Carbonates, oxides and reducible metals	25 ml of 0.04 M $NH_2OH \cdot HCl$ in 25% HAcO	1 h at 95°C, agitating occasionally
3. Bound to organic matter, oxidisable and sulphidic metals	25 ml of 0.02 M HNO_3 + 10 ml 30% H_2O_2 + 3 ml 30% H_2O_2 + 5 ml of 3.2 M NH_4AcO in 20% HNO_3	90 min at 85°C, 1 h at 85°C, continuous agitation 30 min at room temperature
4. Residual metals	5 ml of conc. HNO_3 + 2 ml of conc. HCl + 20 ml H_2O	90 min at 95°C, agitating occasionally

Table 2
Speciation scheme according to Fernández Espinosa (1998)

Metallic fraction	Reagent	Experimental conditions
1. Soluble and exchangeable metals	15 ml H_2O (pH=7.4)	3 h at room temperature. Shaker agitation
2. Carbonates, oxides and reducible metals	10 ml $NH_2OH \cdot HCl$ 0.25 M at pH =2.0	5 h at room temperature. Shaker agitation
3. Bound to organic matter, oxidisable and sulphidic metals	7.5 ml H_2O_2 30% + 7.5 ml H_2O_2 30% + 15 ml NH_4AcO 2.5 M, at pH =3.0	At 95°C until near dryness. Shaker agitation + at 95°C until near dryness. Shaker agitation + 90 min at room temperature. Shaker agitation
4. Residual metals	10 ml (HNO_3:HCl:$HClO_4$) (6:2:5)	5 h at 95°C. Shaker agitation

Table 3

Average concentrations (ng m^{-3}) of the four metallic fractions corresponding to the 11 metals analysed in the 41 samples

Fraction	Metal																					
	V		Pb		Mn		Cd		Ni		Cu		Ca		Ti		Fe		Co		Mg	
	Mean	Range	Mean	Range	Mean	Range	Mean	Range	Mean	Range	Mean	Range	Mean	Range	Mean	Range	Mean	Range	Mean	Range	Mean	Range
1	2.06	(0.31 - 8.26)	1.7	(0.0 - 5.1)	2.42	(0.35 - 7.10)	0.052	(0 - 0.147)	0.57	(0.17 - 1.30)	2.53	(0.5 - 17.3)	259	(80 - 764)	0.24	(0 - 1.91)	9.6	(1.2 - 31.7)	0.103	(0 - 0.205)	17.5	(5.8 - 43.4)
2	1.02	(0.00 - 3.78)	14.5	(1.5 - 39.4)	1.84	(0.32 - 5.70)	0.043	(0 - 0.167)	0.27	(0.00 - 0.77)	0.93	(0.1 - 6.1)	379	(27 - 1337)	0.11	(0 - 0.54)	41.5	(7.0 - 227.9)	0.082	(0 - 0.283)	18.9	(3.3 - 38.7)
3	0.52	(0.00 - 2.05)	15.4	(1.2 - 254.0)	2.51	(0.15 - 26.87)	0.065	(0 - 0.797)	0.40	(0.06 - 0.93)	4.08	(0.3 - 34.3)	306	(0 - 842)	1.38	(0 - 7.10)	67.3	(8.4 - 308.1)	0.035	(0 - 0.768)	102.5	(2.3 - 319.1)
4	0.48	(0.00 - 1.36)	12.1	(2.0 - 154.7)	0.66	(0.00 - 6.82)	0.049	(0 - 0.420)	0.19	(0.00 - 0.74)	2.02	(0.1 - 13.3)	10	(0 - 83)	1.43	(0 - 6.91)	142.4	(0.0 - 630.1)	0.073	(0 - 0.380)	34.3	(0.0 - 80.8)
Sum	4.08		43.7		7.43		0.210		1.44		9.57		954		3.17		260.8		0.293		173.1	

1. Soluble and exchangeable metals; 2. carbonates, oxides and reducible metals; 3. bound to organic matter, oxidisable and sulphidic metals; 4. residual metals.

Table 4

Percentages obtained from the common metals in schemes

applied in both years in the four fractions

| Metal | 1993 Scheme[a] | | | | 1996 Scheme | | | |
| | Fraction | | | | | | | |
	1	2	3	4	1	2	3	4
Fe	5	39	13	43	4	16	26	55
Pb	25	53	18	4	4	33	35	28
Cu	24	41	25	10	27	10	43	21
Mn	53	27	11	9	33	25	34	9
Ni	26	16	38	20	40	19	28	13
Co	56	26	12	6	35	28	12	25
Cd	55	11	13	22	25	21	31	24

1. Soluble and exchangeable metals, 2. Carbonates, oxides and

reducible metals, 3. Bound to organic matter, oxidisable and

sulphidic metals and 4. Residual metals.

[a] The samples were collected at the same twelve sampling sites of the city.

Table 5

Main correlation coefficients among the parameters

Correlated chemical fractions	Coefficients (r)
Pb(f.3), Cu(f.3)	0.86
Ca(f.3), Mn(f.3)	0.83
Cu(f.3), Mn(f.3)	0.83
Cu(f.1), Mn(f.1)	0.82
Cu(f.3), Cd(f.3)	0.82
Ca(f.1), Mn(f.1)	0.81
Cu(f.4), Mn(f.4)	0.78
Mg(f.3), Mn(f.3)	0.77
V(f.3), Ni(f.3)	0.76
Pb(f.3), Cd(f.3)	0.75

Fig. 1. Chemical forms distribution of metals as percentage of the elemental concentration in fine particles.