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Physical speciation of arsenic, mercury, lead, cadmium and nickel in inhalable atmospheric particles

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Abstract. Physical speciation of metals (size distribution), in airborne particles has been studied in 24 areas of Seville (Spain). Urban particles were collected with high-volume sampling systems equipped with cascade impactor and PM_{10} inlets. Particle samples were analysed by acid digestion assisted by microwave using a $HNO_3:HClO_4$ (3:1) mixture. Arsenic was determined by hydride generation atomic absorption spectrometry (HG-AAS), mercury by atomic absorption spectrometry and cold vapour technique (CV-AAS) and inductively coupled plasma atomic emission spectrometry (ICP-AES) was employed to determine lead, cadmium and nickel. Analyses of PM_{10} samples revealed that the highest mean concentration was obtained for Pb, 14.04 ng m^{-3}. Values of 3.42 ng m^{-3} and 2.88 ng m^{-3} were obtained for As and Ni, respectively. The lowest concentrations were obtained for Cd, 0.49 ng m^{-3}, and mainly for Hg, 0.07 ng m^{-3}. Their physical speciation in air concentrations (ng m^{-3}) showed that the toxic elements As and Pb were accumulated in the fine particles less than 0.6 μm ($PM_{0.6}$), as well as the metals Cd and Ni, with high percentages of 74.8, 69.0, 61.3 and 57.5, respectively. Hg constituted a lower percentage of 40.4%. The results in mass concentrations (mg Kg^{-1}) demonstrated that Pb and Cd contents were clearly higher in fine particles between 1.3 and 0.6 μm than in $PM_{0.6}$. The

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size interval where Hg contents were higher than in $PM_{0.6}$ (4.9 to 0.6 µm) corresponded to a fine and also a coarse mode, meanwhile Ni presented similar percentages between all size ranges. However, As is mainly accumulated in $PM_{0.6}$ in both air and mass concentrations, revealing that it constitute the element more hazardous in relation to its size distribution.

Keywords: Size distribution; Arsenic; Mercury; Airborne particles; PM_{10}; Speciation; Microwave.

1. Introduction

Atmospheric pollution by heavy metals in particles is one of the most worrisome problems nowadays in the scientific community. Particulate matter has a direct incidence on the health through the respiration because of their small size and the heavy metals composition, which have influence in biochemical mechanisms, especially because they are bioaccumulable. Fine particles are more easily transported to large distances and they can stay in the air in a prolonged manner depending on the meteorological situations and size distribution [1]. Size distribution of particles and metals give information for studies of transport process, effect of meteorology and sources study. For instance, it well known that elements associated with natural sources, such as soil and ocean, are usually found in coarse particles, while elements emitted from anthropogenic sources are associated with fine particles [2]. The relation between meteorology and particle size distribution has also been the subject of numerous recent and earlier works, as in Manchester [3], Helsinki [4] and in a Mediterranean zone of France [5].

The degree of bioaccumulation and bioavailability depends on the physical and chemical composition of particles. Conventional metal determinations are still carried out

today by methods that lead to total concentrations. These total concentrations are nowadays determined only in a few cases in TSP (total suspended particles). These determinations should be done with particles speciated by size [6, 7], such as PM_{10} or $PM_{2.5}$ and, less frequently, by impactor systems [8, 9]. Therefore, knowledge of particle size is vital in understanding the effects on human health. The degree of respiratory penetration and retention is a direct function of the aerodynamic particle (aed) diameter [10]. In general, only particles less than 10 or 15 μm in size reach the lower respiratory tract from the nose to the alveoli [11]. Particles with a diameter higher than 5 μm are filtered in the nose for the most part, while those less than 1-2 μm predominantly gets deposited in the alveolar regions of the lung, where the absorption efficiency for trace elements is 60-80% [12]. They could affect lung physiology, especially if the particles contain biologically available toxic elements, such as heavy metals. Knowledge of the size distribution of these metals using cascade impactors (physical speciation) and inlets (PM_{10}) is the aim of the current research. This way, an objective of this work was to assess an analysis methodology for determine heavy metal concentrations in airborne particles based on physical speciation techniques. These techniques are also useful in characterising and identifying sources of heavy metals [13].

The other objective of this work is to propose a cut-point for the future PM inlets manufactured. Actually, the American Environmental Protection Agency [6] and the European regulatory laws will create soon mandatory measurements on $PM_{2.5}$, breathable particles [14], which shows a clear inclination to study smaller particles. Actually, PM_{10} inlet is the only reference method that is exists. PM_{10} inlets used by us and the cascade impactor systems used in our physical speciation techniques give wide information about different size fractions of particles and their chemical composition. The evaluation of the size distribution with the impactor system device allows establish the relationship

between the different size fractions and the different cut-points of inlets (PM_{10}, $PM_{2.5}$ or PM_1) along a single sampling, without needing different inlets for each size fraction. The comparison between PM_{10} results and physical speciation of heavy metals constitute an objective of the current investigation in order to propose a different cut-point for the future.

Besides, making demands on the new European Framework Directive of Evaluation and Management of Ambient Air Quality [15]. Because of these demands our research group set up a study on speciation of arsenic, mercury and other heavy metals to conform to the law. Various daughter directives were published, such as that concerning to PM_{10} (particles less than 10 micrometers) and lead [16]. Actually there is a recent proposal for the Fourth Daughter Directive relating to arsenic, mercury, cadmium, nickel and polycyclic aromatic hydrocarbons in ambient air [3]. For example, no later than 31 December 2003 the European Commission will submit a report, based on knowledge acquired in the application of the Directive 99/30/EC (article 10), to the European Parliament and the European Council. The Junta de Andalucia, our regional government, through its environmental office (Consejeria de Medio Ambiente) finances research for the Andalusian Universities, focusing the results on the annual reports they present to the European Commission. Our particular group is one of those collaborating with the Junta for this mission, offering analytical methods to the European Community to measure pollutants and in return being able to investigate new analytical strategies to feed into the scientific community. In relation to these two engagements, this work presents the results of composition of airborne particles by heavy metals, focusing the interest of results on arsenic and mercury. Both metals were no measured before using our physical speciation techniques. Even the metal lead, measured previously by us when leaded gasoline was still

used in cars [2], present a special interest because actually it cannot come from a traffic source due to the use of unleaded gasoline.

2. Experimental

2.1. Sampling network design

A sampling network of sampling stations was designed at the city of Seville (37°23' N, 5°58' W, Fig. 1 and Table 1), the largest and most air polluted city by traffic of Andalusia (Spain) [17]. The network was spanned including 24 sampling sites, twelve more than in our previous network [2], covering all city districts and some peripheral zones and towns. Two samplers were rotated and located near the typical emission sources of the city, such as highly trafficked streets, some big local industries and zones nearby to unpaved soils, as well as in locations with cleaner air. Consequently, the different sampling points were classified into three categories: sites under influence of industrial emissions, station under the influence of vehicular emission and peripheral station under the influence of resuspended soils. This way, information about a higher number of sampling sites than the number of sampling stations of our Local Air Monitoring Network of Seville was obtained in the city.

2.2. Samples collection system

Atmospheric particulate matter was collected with two standard high-volume samplers MCV, model CAV-A/HF [18], one of them was equipped with a five-stage standard cascade impactor plus a backup filter MCV, model IC/CAV, and other was coupled with a PM_{10} inlet (MCV, model PM_{10}/CAV). PM_{10} inlet was used to collect all particles less than 10 micrometers (aed) and the MCV mark was inter-compared with the reference PM_{10} inlet of the EN 12341 European Norm. Cascade impactor system

separates the particulate matter following aerodinamic equivalent cut-off diameters (aed) at 50% efficiency: Stage 1, > 10 μm, stage 2, 10-4.9 μm, stage 3, 4.0-2.7 μm, stage 4, 2.7-1.3 μm, stage 5, 1.3-0.6 μm and stage 6, < 0.6 μm (0.6-0.01) (Backup). Both sampling systems were set at a flow rate of 68 $m^{-3}h^{-1}$, according manufacturing specifications. The set of filters used as collection media (Whatman GF/A) were constituted of five cut filters (14.2 x 14.2 cm) for stages of cascade impactor and a complete non-cut filter (24.5 x 20.3 cm) for the backup and PM_{10} inlet was used.

PM_{10} inlet gives an only value of particle and metal concentration in each sampling. Impactor separator gives different particle and metal concentrations in each sampling. These different concentrations could be expressed simply as percentage regarding the total concentration, that is, the sum [8], or expressed as various types of normalised concentration [18]. This way, the analytical data of size distribution of particles and physical speciation of metals was obtained with the impactor system.

A total of 93 samples were collected, being 48 samples collected with cascade impactor and 45 samples collected with PM_{10} inlet. Sampling period was from January 2000 to June 2001, during 18 month, so, samples were usually taken on different days each week, obtaining samples of every day of the week, therefore, in different meteorological and environmental conditions. Sampling periods were from 0:00 a.m. to 23:59 p.m.

2.3. Analytical procedure

Before the analysis of samples, filters used for particle collection were dried, before and after weighing, in a high-volume desiccator under 5% R.H. for a 48-h period. Operations of conservation, drying and weighing took place in a dark room at 50±5 % R.H, a temperature of 20±1 °C was controlled by a heating-cooling system [2]. Care was taken in handling the sampled filters in order to avoid contamination problems using a vertical

laminar airflow cabinet with a HEPA filter Indelab, model IDL-48V, thereby ensuring air cleanliness standards of class 100 according to the US-Federal Standard 209E [19].

Filters were placed in closed teflon vessels with 15 ml of HNO_3-$HClO_4$ v/v (3:1) and digested in a microwave oven Millestone, model Ethos 900 with a specific digestion programme. After digestion and cooling, sample solutions were transferred into sterile tubes. Residual particles became colourless and filters were completely whites, with regard to the previous system used: heating with water bath [2].

Since individuals blanks were not available for each filter used for sampling, a set of unexposed filters for each type of filter was analysed as blanks using the same procedure used for samples. The mean unexposed filters value were determined and subtracted from each sample to obtain the best estimate of each element in the particulate matter. Table 2 shows the limits of detection (LOD) of the method (obtained from blanks values and their standard deviations) and the instrumental limits of detection (obtained from analytical calibrations).

The accuracy of the method was previously checked when this was validated by analysis of a NIST reference material SRM 1648 [21,22,25]. The standard addition method was used to validate the mercury determination, since this element was not present in the SRM 1648 certificate. The results of recovery correspond with 18 different test applied to the SRM (Table 3) showing that recoveries of all elements were into the intervals recommended by the A.O.A.C. A gold solution was used as internal standard to spike samples, blanks and reference material and to check the correct quantification of the elements. Previously, it was studied that gold was not presented in urban air and its presence within the teflon vessel had no influence on analytical determinations of the other metals. All ultrapure reagents and standards were supplied by Merck and distilled water was of Milli-Q grade obtained from a Waters-Millipore apparatus, model Plus.

Acid solutions were analysed for lead, cadmium and nickel by inductively coupled plasma atomic emission spectrometry (ICP-AES), using a Fisons-ARL 3410 sequential multi-element instrument. The standard operation condition of this instrument are summarised as follows: the carrier gas, coolant gas, and plasma gas is argon at 80 psi of pressure, the carrier gas and plasma gas flow rate are 0.8 l min^{-1}, the coolant gas flow rate is 7.5 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}. In order to avoid errors in results due to the effect produced by the different viscosity and density of the acid matrix of samples on the ICP nebulisation, calibration curves have been made with the same acid matrix.

Arsenic was analysed by hydride generation atomic absorption spectrometry (HGAAS) and mercury by cold vapour technique (CV-AAS) using a Perkin-Elmer 3100 atomic absorption spectrometer with hydride generator Perkin-Elmer model MSH-10. The standard operation condition of this instrument are summarised as follows: the carrier gas is nitrogen at 36 psi of pressure, stock solution of reductant containing 3% m/v NaBH$_4$ and 1% m/v NaOH assuming the reduction of As(V) species to As(III) and the generation of hydrides corresponding to As(III) formed; reaction medium containing 1.5% HCl m/v [20-24]. The atomiser used was a quartz T-shaped tube, heated with an air-acetylene flame for arsenic and flameless for mercury determination. The detection wavelength was 193.7 nm for arsenic and 253.6 nm for mercury.

3. Results

3.1. Particle levels in air

Mean values of PM$_{10}$ samples in the 24 sampling sites of Seville were shown in Fig. 2. Average of PM$_{10}$ levels over the sampling period (18 month) was 41.8 µg m^{-3}. This

concentration exceeds even the annual limit values of PM_{10} for the protection of human health (40 μg m^{-3} for 2005 and 20 μg m^{-3} for 2010) established by the new European Framework Directive of Evaluation and Management of Ambient Air Quality [15]. In addition, in some sampling sites, such as stations 2, 6, 10, 11, 14, 18, 20, 21 and 23, the concentrations exceeded the 24-hour limit value for PM_{10} (50 μg m^{-3}), exceeding in more than the permitted 35 annual exceedances that the directive will accept until 2005 (7 annual exceedances until 2010).

In relation to the particle size distribution, the impactor fractionation shows (Fig. 3) typical two size-dependent log normal distributions. One mode corresponds to the accumulation mode, a fine mode below 1.3 μm aed, and other one corresponds to mechanical erosions, a coarse mode around 10 μm aed (stages 1 and 2). Therefore, the more abundant particles in air are the finest sizes, constituting 48.4% of the total suspended particles. This constitutes a higher harmful risk because these fine particles can reach and deposit even into the alveolar region of the lungs [26]. Coarse particles > 4.9 μm represent 33.9%. These are usually attributed to an earth crustal origin, and they can be deposited on the external respiratory tracts, so they represent a minor risk for human health.

3.2. Heavy metal concentrations in PM_{10}

In PM_{10} samples (Fig. 5), the highest concentration was obtained for lead 14.04 ng m^{-3}. This value is lower than other obtained some years ago when leaded gasoline was still used [27]. Arsenic with 3.42 ng m^{-3} and nickel with 2.88 ng m^{-3} presented medium levels. The lowest concentrations were obtained for cadmium 0.49 ng m^{-3} and mercury 0.07 ng m^{-3}.

The average annual limit value for lead in PM_{10} particles proposed by the 99/30/EC EU-Directive is 500 ng m^{-3}. This limit value was not reached by the mean value for the sampling period. Only a few numbers of exceedances were occurred in various samples in industrial sites. In relation to the limit values of the proposal for the Fourth Daughter Directive [28], the thresholds for the other metals averaged over a calendar year are 6 ng m^{-3} for arsenic, 4 ng m^{-3} for cadmium and 20 ng m^{-3} for nickel. Our experimental values were no reached these threshold values for any metal. Only arsenic is close to its threshold, approximately half the EU-value. However, the results are different when the comparison were done with the values of the WHO Guidelines for Air Quality [29].

WHO proposes a unit risk of 1.5 x 10^{-3} (μg m^{-3})$^{-1}$ for arsenic. This unit risk is the extra risk of contracting lung cancer, if continuously exposed to 1 μg m^{-3} for a lifetime. Translating this unit risk into an annual average concentration that equates to a lifetime risk of one in a million, gives a concentration of 0.66 ng m^{-3}. The US EPA recommends a unit risk of 1.8 x 10^{-3} (μg m^{-3})$^{-1}$ for cadmium. By accepting an excess risk of one in a million this results in a concentration of 0.24 ng m^{-3}. The WHO recommends a unit risk of 3.8 x 10^{-4} (μg m^{-3})$^{-1}$ for nickel. Based on this number an excess lifetime risk of one in a million corresponds to a concentration of 2.5 ng m^{-3}. Based on a LOAEL-approach (Lowest Observed Adverse Effect Level) of the WHO Air Quality Guidelines for Europe (WHO, 1987) for mercury it was found that an annual average concentration of 50 ng m^{-3} of elemental mercury should not be exceeded in ambient air. Therefore, average concentrations of arsenic, cadmium and nickel are above their Unit Risk (U.R.) values based on cancer.

3.3. Physical speciation results

The study of the metal abundance in different particle sizes has a notable toxicological interest in fine particles. The mean size profiles of metals obtained with the impactor are

shown in Fig. 4. All metals were highly associated to fine particles. The results of distribution expressed as percentages were 74.8% for arsenic, 69.0% for lead, 61.3% for cadmium, 57.5% for nickel and 40.4% for mercury. These percentages were obtained from the concentrations expressed in inmission levels or air concentrations (ng m^{-3}), but it is also interesting to discuss the results obtained from concentrations expressed in metallic richness or mass concentrations (mg Kg^{-1}).

Results obtained by metallic richness present some differences with those found for inmission level. The mass concentration unit for air pollution is useful and constitutes an important tool for the knowledge of the heavy metal behaviour. Generally, profiles observed for all the elements showed differences. Maximum percentages were obtained in particles between 1.3 and 0.61 μm for cadmium (29.7%) and lead (29.5%). Nickel presented a uniform distribution along all size ranges. Mercury shows a different profile than the other studied elements, with a maximum value (12.6%) in particles between 4.9 and 2.7 μm and similar values in particles between 2.7 and 0.6 μm. Therefore, mercury was mainly distributed in a size range between 4.9 and 0.6 μm, including fine and also coarse particles, indicating the presence of earth crustal resuspensions. Besides, the lowest percentage was found in the finest particles. However, arsenic presented the maximum value (31.3%) on the finest fraction (< 0.6 μm), like in the inmission study. Therefore, arsenic contents predominated in PM$_{0.6}$ in both air and mass concentrations.

4. Conclusions

Interesting results from a study of different size distributions (PM$_{10}$ and impactor) of heavy metals were obtained due to the use of a wider sampling network than in previous works. Consequently, a greater number of particle samples were collected during a large sampling period of eighteen months, therefore much information was obtained.

The annual mean value and exceedances of PM_{10} observed in Seville were higher than those established in the 99/30/EC Directive. However it is well known that these high concentrations are also due to contributions of intrusive Saharan particles. One should keep in mind that the results of size distribution pointed to fine particles less than 0.6 μm as those more dangerous for lungs when they penetrate until the alveolar region. Therefore the study of physical speciation of heavy metal constitutes a necessary method to obtain crucial analytical information.

Levels of heavy metals in PM_{10} showed that lead was still the more abundant in the air although leaded gasoline had disappeared. Any metal no reached the limit values proposed by the EU-laws, although arsenic, cadmium and nickel are above the Unit Risk (U.R.) values based on cancer of the WHO. Only arsenic is close to its threshold and its physical speciation showed that it was accumulated in the finest particles in both air and mass concentrations, revealing that it constitutes the element more hazardous. Hg constituted a lower percentage of 40.4% because its size interval shows an accumulation in both fine and coarse particles, due probably to the accumulation in soil particles coming from an old thermal central that no exits since a lot of year ago.

Because all these evidences, $PM_{2.5}$ and even PM_1 inlets should be proposed as reference methods for monitor these pollutants in air.

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Table 1

Description of the 24 sampling stations corresponding to the sampling network of Fig.1

Number	Site	Number	Site
1	Art High School	13	School of Informatics Engineering
2	'Macarena' Public School	14	Air Force Clinic
3	'Esperanza' Public School	15	Polytechnic High School
4	Office of 'Hermandades y Cofradias'	16	'I. S. Mejias' Public School
5	The Andalusian Ombudsman	17	'S. Angel de la Guarda' Public School
6	School of Applied Arts	18	The SE-30 Road Maintenance Centre
7	Chemical Research Institute (IIQ-CSIC)	19	Transfer Centre of Urban Residues (LIPASAM)
8	'Llanes' Secondary School	20	'Tartessos' Secondary School
9	'Baltasar de Alcazar' Public School	21	'Camas' Secondary School
10	'Borbolla' Public School	22	'Carlos V King' Public School
11	'Esperanza' Neighbours Association	23	'Cortijo de Cuarto' School of Agricultural Engineering
12	Faculty of Chemistry	24	'A. M. Mateo' Public School

Table 2

Limits of detection of method and instrumental limits of detection for an air volume of 1632 m^3

Element	LOD of method (ng m^{-3})	Instrumental LOD (ng m^{-3})
As	0.025	0.002
Hg	0.027	0.002
Pb	0.940	0.283
Cd	0.199	0.112
Ni	0.305	0.240

Table 3.
Mean values of recovery obtained from the accuracy study with the SRM 1648.

Elements	Recovery (%) (n=18)	R.S.D. (%) (n=18)	Confidence Interval (P=0.05)	A.O.A.C. Criterion
Arsenic	99.9	2.6	3.3	90-107
Mercury	99.1	3.5	2.1	80-110
Lead	95.3	2.6	1.3	95-105
Cadmium	110.0	3.7	1.8	80-110
Nickel	86.0	4.2	2.1	80-110
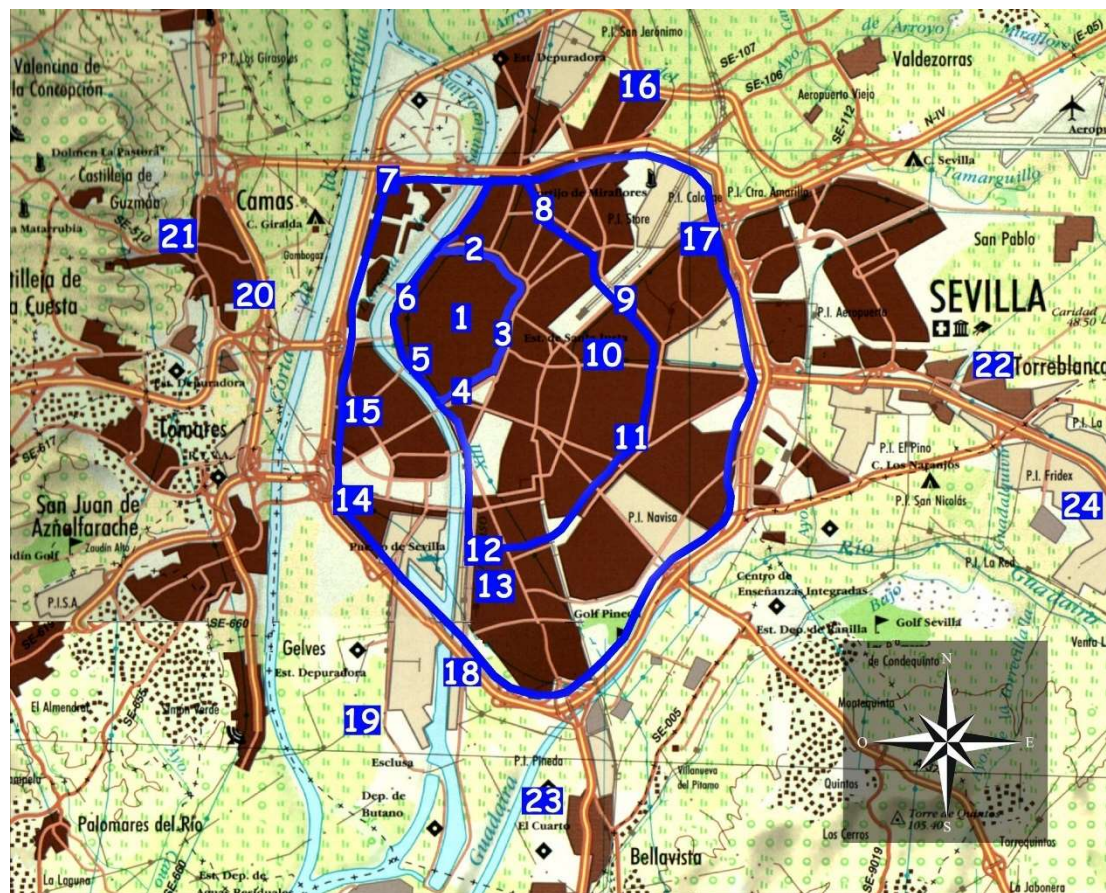
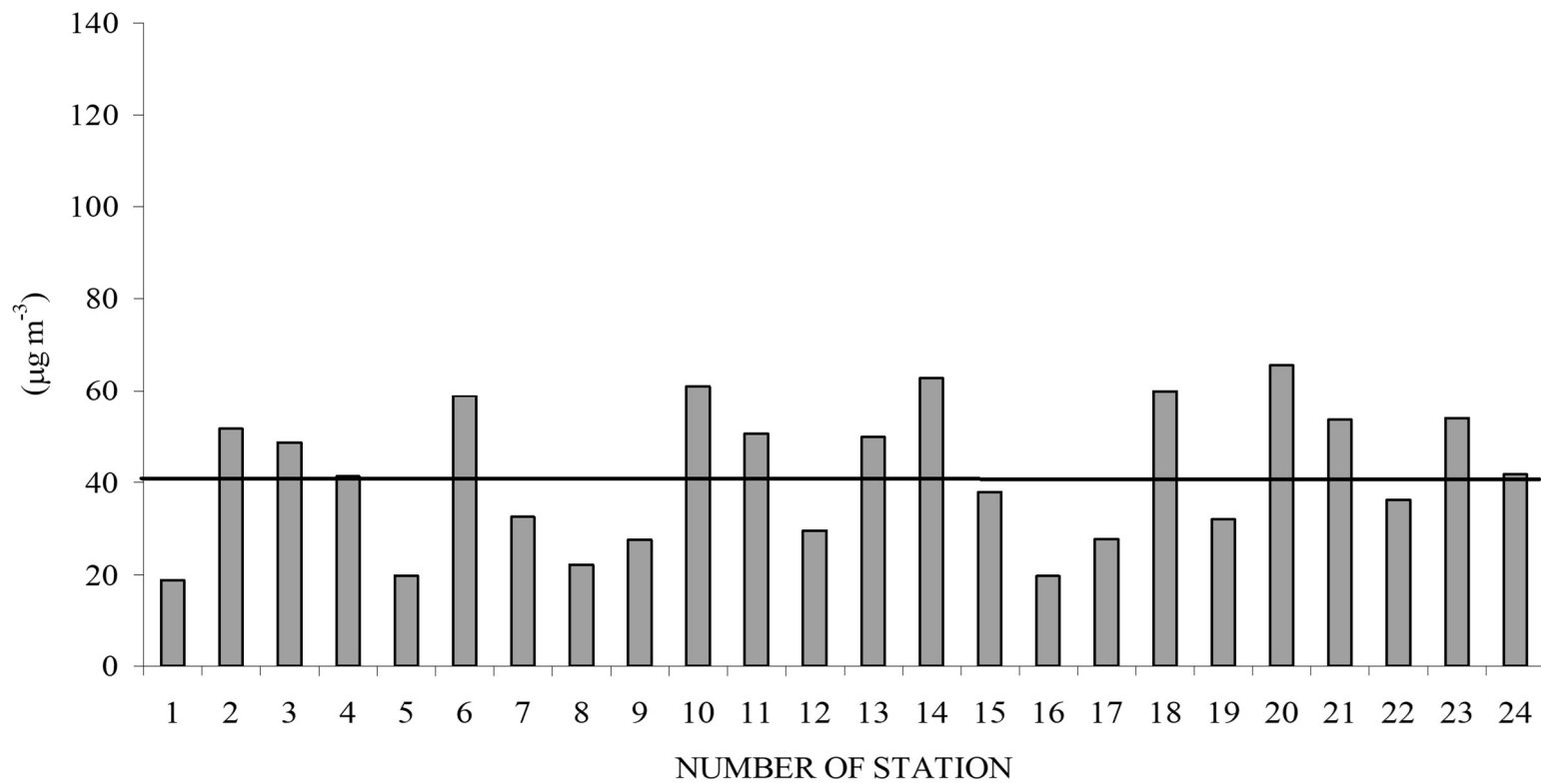Fig. 1. Sampling network designed in Seville: location of the 24 sampling stations.

Fig. 2. Values of PM$_{10}$ obtained at the different sampling stations of Seville: horizontal line represents the average value.
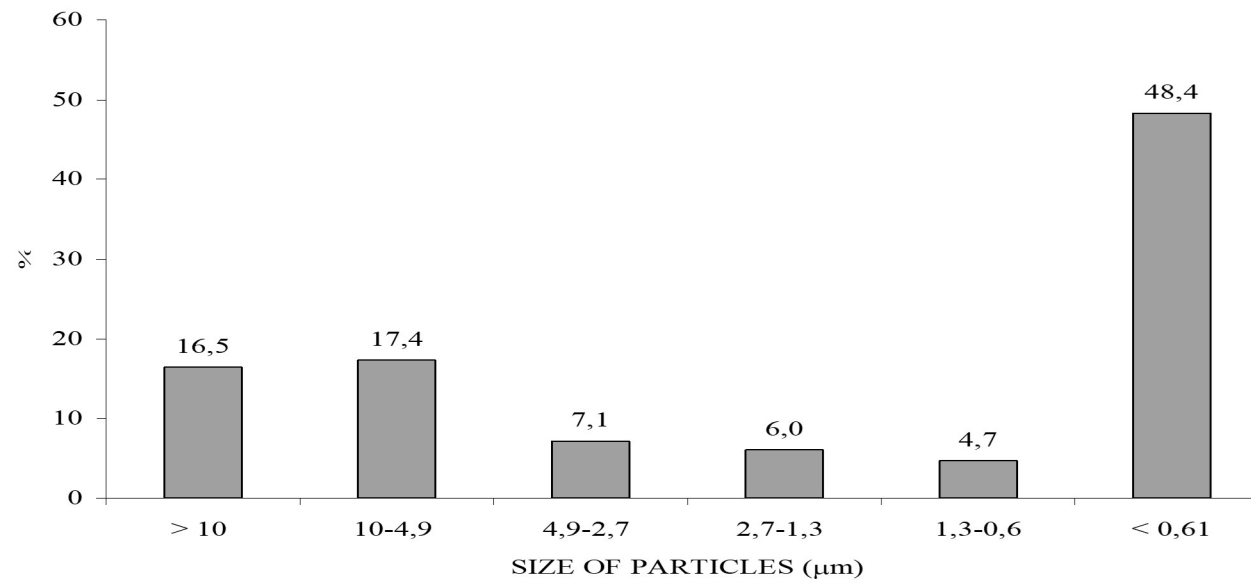
Fig. 3. Particle size distribution corresponding to the sampling period expressed as percentages of the total particles collected.
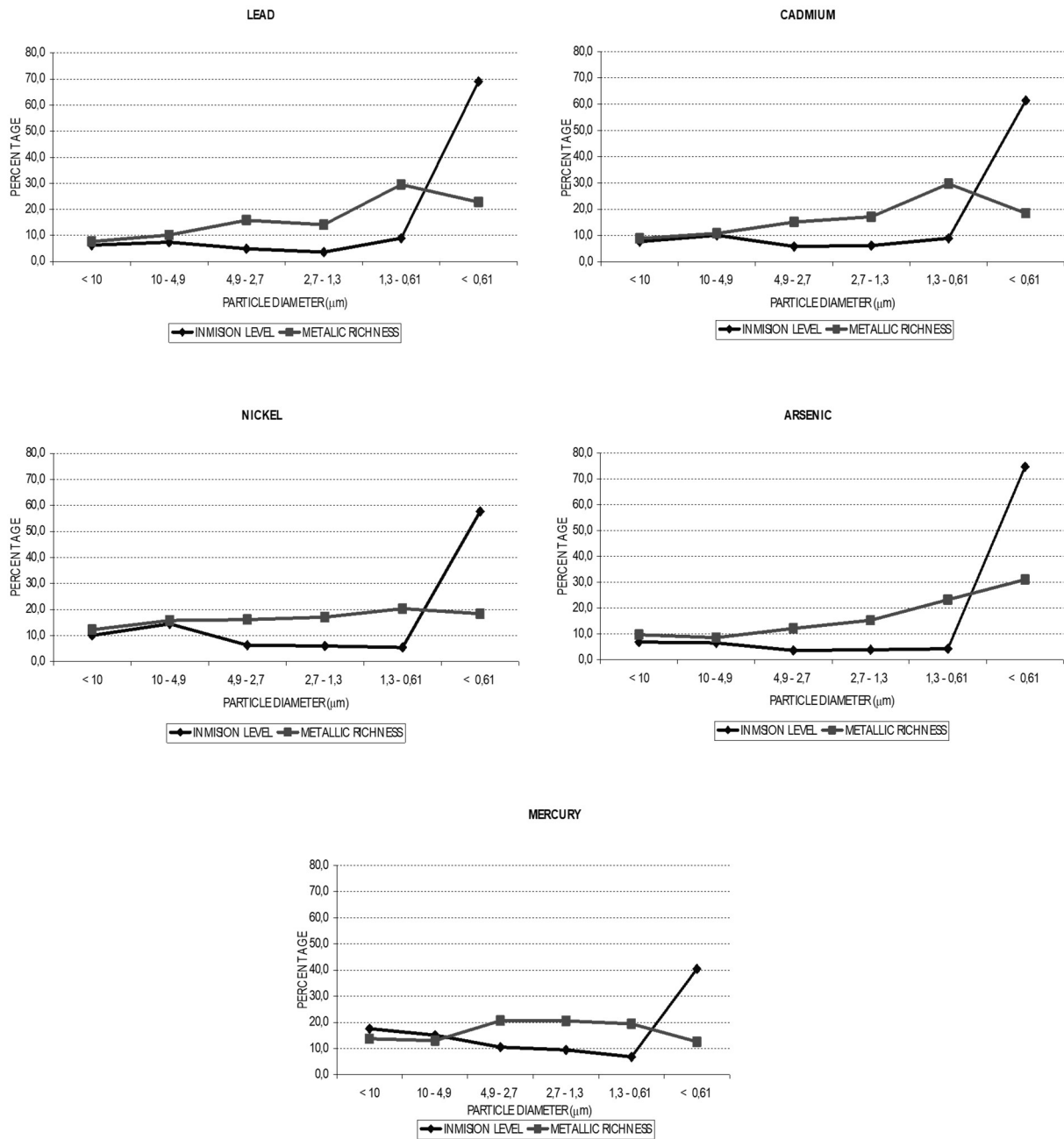
Fig. 4. Physical speciation of metals expressed in inmission level (ng m^{-3}) and metallic richness (mg Kg^{-1}).
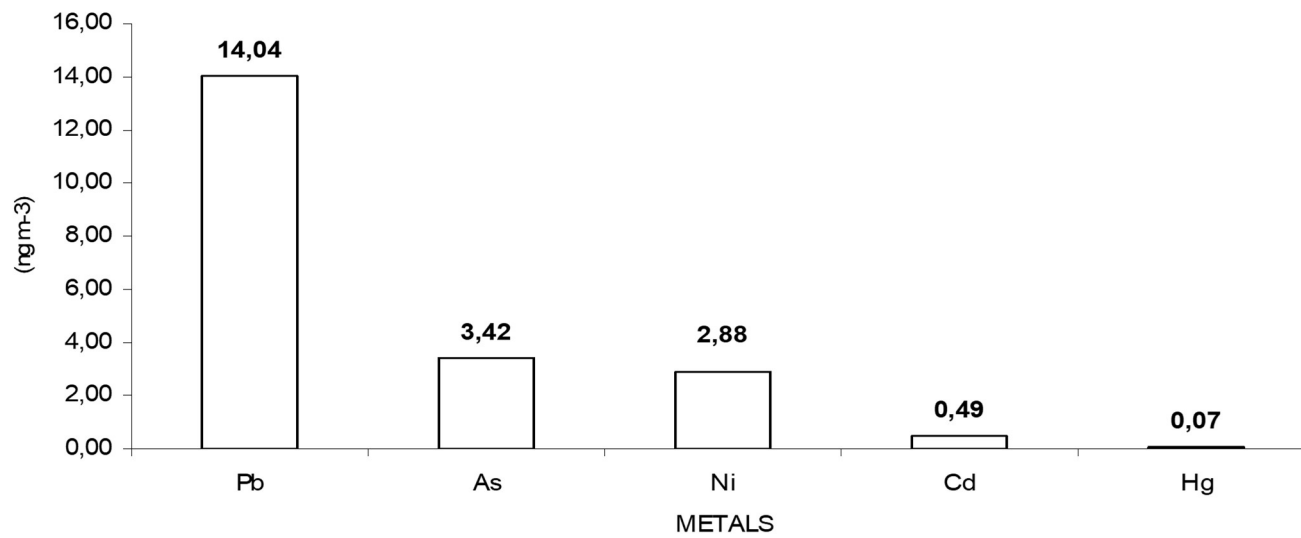
Fig. 5. Mean concentrations of metals obtained in PM_{10} samples