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A study of the atmospheric traffic pollution based on the physical and chemical speciation of heavy metals

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Abstract A series of 83 samples of atmospheric particles were collected at a representative traffic site in a Mediterranean city during one year. Urban particles were collected on quartz filters with a high-volume sampler coupled with a cascade impactor, which separates particles into six size ranges: 10-4.9-2.7-1.3-0.6 μm. Total metal contents, their distribution by size and chemical form concentrations in particles less than 0.6 μm were determined. The chemical speciation scheme consisted of four fractions: soluble and exchangeable metals; carbonates, oxides and reducible metals; bound to organic matter, oxidisable and sulphidic metals; and residual metals. The samples were analysed by ICP-AES. Gaseous pollutants, traffic intensities and meteorological primary data provided by the atmospheric and traffic networks were statistically related to analytical data. Analytical results of physical and chemical speciation singled out Ba as valid tracer of vehicular traffic instead of Pb. Other important relation was found between Pb and Cu. Cd was also associated with traffic in this high trafficked site, however, Ni was associated with the influence of near industrial combustion. Physical speciation of lead showed that the major risk was found in fine particles less than 1.3 μm, where the particles between 1.3 and 0.6 μm represented the size fraction of particulate matter more enriched in lead and particles less than 0.6 μm were the fraction of airborne particles more abundant in the urban air. Result for Cd size distribution was more similar to lead profile than for Ni. Chemical speciation results showed that special attention have to take with Ni and Cd concentrations because of their high potential bioavailability, mainly the high solubility of chemical forms in which Ni was presented in the finest particles.

Keywords Heavy metals - Airborne particles - Traffic pollution – Analytical characterisation – Chemical speciation – Size fractionation

Introduction

Particulate matter has a direct incidence on the health through the respiration because of their small size and heavy metals 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]. The degree of bioaccumulation and bioavailability depends on the characteristic 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. These determinations should be done with particles speciated by size [2,3], such as PM10, PM2.5 or PM1 and, less frequently, by impactor systems [4,5]. In relation to the chemical aspect, it is often necessary to quantify metallic chemical forms, such as specific species or a set of common species. The bioavailability, solubility, geochemical transport and cycles for metals depend heavily on physical and chemical speciation. Thus, total determinations are many times insufficient and speciation is an answer to finding the real metal activity in the environment, implying a new viewpoint for analytical control.

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Size distribution of metals (physical speciation) determines the concentration of heavy metals in different particle size ranges [6]. The composition by heavy metals varies because of the different sizes of airborne particles. These variations are due to the sources that the different particles come from. The physical and chemical transformation processes in the air also cause variation of particle size. Physical speciation determines the way in which particles are transported through distances and lifetimes in the air. Besides, particle size determines the place of deposition in the human respiratory tract; that is, the degree of penetration. The needs for speciation analysis in environmental field constitute new trends in analytical chemistry [7,8]. In airborne particle samples, chemical speciation of metals determines the concentration of heavy metals in different chemical forms, according to their potential bioavailability to the human body through the lung. So, one can determine the contribution to the total metal concentrations of soluble/exchangeable metals, which are the most bioavailable to lung tissues in the alveolar region. The most available chemical forms and species to the human body are those most harmful, mainly when the heavy metals are toxic and associated with fine particles. Fine particles can penetrate to the alveolar region, where the exchange between oxygen and carbon dioxide is the entry to the blood stream.

In Europe, the fifth action programme of 1992 on the environment envisages amendments to existing legislation on air pollutants. The general aim of the 96/62/EC Framework Directive is to define the basic principles of a common strategy [9]. The list of atmospheric pollutants of this directive includes sulphur dioxide, nitrogen dioxide, carbon monoxide, ozone, fine particulate matter such as soot (including PM10), suspended particulate matter (TSP), lead, cadmium, arsenic, nickel, mercury, benzene and poly-aromatic hydrocarbons. Various daughter directives have been already published in the Official Journal of the European Communities, such as the Directive 2002/3/EC for ozone, the 2000/69/EC for benzene and carbon monoxide and the 99/30/EC for the rest. The last of them establishes the limit values for sulphur dioxide, nitrogen dioxide and oxides of nitrogen, particulate matter and lead in ambient air. Actually there is a proposal for the Fourth Daughter Directive of the European parliament and of the council relating to arsenic, cadmium, mercury, nickel and polycyclic aromatic hydrocarbons in ambient air.For the air pollutants the European Community has to measured, sampling and analysis are relatively easy by automatic monitoring, except for determining the content in particles, such as heavy metals or polycyclic aromatic hydrocarbons (PAHs). There isn't an automatic method to monitor these compounds; therefore, manual methods have to be used.

Regarding to the 99/30/EC, for instance, 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. In our particular case, it shall submit on the results of the most recent scientific research concerning the effects on human health of exposure to different fractions of particulate matter and lead, and on the progress achieved in methods of measuring and otherwise assessing concentrations of particulate matter in ambient air. 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 these annual reports that the regional government have to present to the European Commission. Our particular research group is one of those collaborating with the Junta for these projects, offering analytical methods to measure pollutants and in return being able to investigate new analytical strategies to feed into the scientific community. Two important researches have been finished; one of them in 1998 and the other in 2003. The first provided sufficient amount of data to submit the report above mentioned. The last project will be reported later on.

This way, the aim of this work was to assess a method to analyse heavy metals using our analytical method based on physical and chemical speciation techniques. These techniques are

useful in characterising and identifying sources of heavy metals. It is the first time that we presents the results of the simultaneous application of both physical and chemical speciation techniques to the same samples collected in a large campaign during one year in a representative traffic site. Therefore, the objectives consisted in to apply the information obtained with analytical methods of physical and chemical speciation to the relationship with the traffic pollution, using information about traffic intensities, as well as levels of other air pollutants and meteorological primary data obtained by automatic gauges. All results will be also useful for characterise the air pollution of a traffic site. Actually, lead emissions from cars in Spain has not existed and new elements as tracers of vehicular traffic should be find and proposed. The current research corresponds to a sampling campaign carried out when the unleaded and leaded gasoline were usually used by cars before leaded gasoline was no longer sold. Therefore, samples collected during this sampling period constitute an important opportunity to find metals originated from traffic correlated with lead.

Experimental part

Methodology

A method to study a determined type of pollution source, such as traffic, should comprise rigorous requirements in the sampling stage, in the analytical measurements and in the treatment of results.

Characterisation of air pollution at a traffic site needs to cover at least one year of sampling campaign, as this one did. This campaign recorded every month, every week and every day of the week including holidays and vacations. Besides, a representative area of high vehicular traffic was necessary for this work. The sampler used to collect airborne particles was placed at the top of an automatic gauge belonging to the Regional Air Monitoring network of Andalucia, a subset of the State and Local Air Monitoring (SLAM) network [10]. Therefore, ambient data, such as those for SPM (suspended particulate matter), SO_2, NO_2, CO and O_3 were provided. Meteorological data, such as for rainfall, ambient temperature, atmospheric pressure, wind speed, wind direction and solar radiation, were also provided by this automatic gauge. The automatic gauge used was at the site in Seville of the most intense traffic. Traffic data were provided by the Seville Traffic Control Centre (SETCC) of the city council.

The analysis stage of the method consisted of three phases. The first one was the weighing procedure to determine Total Suspended Particles (TSP) and size Distribution of Total Suspended Particles (DTSP). From the different particle size concentrations, indicative values of PM10, PM2.5 and PM1 concentrations were obtained and assessed [11,12]. PM10 was obtained from the sum of fractions B to F, PM2.5 from the sum of the fractions D to F and the PM1 was obtained from the sum of the fraction E and F. Our comparisons were done using the limit value for PM10 of the European Directive 99/30/EC. The second phase was the analysis of metals to determine the Total Metal (TM) concentrations (in total suspended particles) as well as their size distribution, determining the Fractionated Metal (FM) concentrations by physical speciation. Although more than 20 elements were investigated, the study centred mainly on lead, nickel and cadmium, objectives of the EU Framework Directive and on the elements more correlated with them. Other interrelated elements are discussed in the paper. The comparisons were done with the limit value for total lead concentration of the EU-Directive 99/30/EC, as well as with the proposed limit values for nickel and cadmium of the Proposal for the new Directive relating to heavy metals and PAHs in ambient air. Also values and ratios between TSP, PM10, PM2.5 and PM1 were evaluated. The comparisons were also done with the unit risk based on cancer of the World Health Organisation for metals [13]. The third phase of the method is the most interesting: the application of a validated operational scheme or sequential extraction to determine the Speciated Metal (SM)

concentrations by chemical speciation on the fine size fraction of particles [14].

The major work on metal speciation has been carried out in environmental samples [15] and biological materials. Many studies were done in soil and sediment. Only a few papers have been published on metal speciation in airborne particulates [16]. One distinguishes between 'specific' and 'operational' speciation, the first depends on direct determination of specific chemical forms, and the second depends on the effect of applying successive reagents to the sample. Methods for specific speciation generally involve the use of spectroscopic, chromatographic or hyphenated techniques [17]. Operational speciation defines different fractions of the total metal content according to expected characteristic behavior of the different chemical forms present in the sample [18]. Thus, the scheme in which the sample is treated sequentially with a series of extraction reagents is employed to separate species. Since the reagents are chosen according to bioavaibility criteria, then the metal species analyzed represents those that living creatures can assimilate. Finally, combination between specific and operational speciation techniques is enable in other works [19].

Combination of the results of size distribution of metals and their chemical speciation was the main useful innovation in diagnosing the level of health risk. This innovation constitutes a first aspect of the strategy to approach a new way of doing an analytical control of metallic pollution.

In relation to the treatment of results, another aspect of the new strategy was the use of the concentration unit in mass:

$$\text{Metallic richness}\left(\text{mg kg}^{-1}\right) = \frac{\text{Mass of metal (mg)}}{\text{Mass of particles (g)}} \times 10^3$$

This concept, different to the air concentration unit (inmission levels) is named 'metallic richness', different from the air concentration unit.

$$\text{Inmission level } (\text{ng m}^{-3}) = \frac{\text{Mass of metal (mg)}}{\text{Air volume } (\text{m}^3)} \times 10^6$$

Consequently,

$$\text{Metallic richness } (\text{mg kg}^{-1}) = \frac{\text{Inmission level } (\text{ng m}^{-3}) \times \text{air volume } (\text{m}^3)}{\text{Mass of particles (g)} \times 10^3}$$

This is useful for comparing the level of metallic pollution in air at different sampling sites, where samples are collected on different days, counteracting the effect of the different meteorological conditions that provide various amounts of particles (mainly rainfall and wind speed). Additionally, studying this mass concentration unit is useful when results of physical speciation of metals are compared in the two units. The determination of ambient, meteorological and traffic data consisted of integration of the period corresponding to the sampling period. The final data were averaged values during the sampling period. For the rainfall parameter, hours of sun and traffic intensities, the final data are sum values during the sampling period. Characterisation showed the following results: average results during the sampling year with other basic statistical parameters (minimum, maximum, relative standard deviation), difference between weekdays (Mondays to Fridays) and weekends (Saturdays and Sundays) and results on the seven days of the week. Finally, interrelation between the analytical results and the traffic, meteorological and ambient parameters are shown through correlation studies. In brief, these concrete requirements in sampling, analysis and in the treatment of results constituted new aspects never included together in any previous works.

Measurement sites and particulate sampling

The sampling campaign was done in Seville (37°23' N and 5°58' W), the largest and most polluted city of Andalusia (Spain), mainly produced by traffic [20]. Our group has studied the urban pollution in the atmospheric particulate matter in the city in various previous works since 1982.

The metal pollution was also determined in 1993 by the analytical focus of the total metal concentrations and in 1996 through chemical and physical speciation. After the results from these twelve areas were studied, the two most polluted sites were selected, together with the assessment by agents of the government, for an annual campaign. One site corresponded to a representative industrial zone, in the only interior Port of Spain, the 'Puerto de Sevilla'. The other site corresponded to a sector with high vehicular traffic, which constitutes the site selected for the current work. Although it is far from the historical city centre, the surroundings of this site are in a densely populated area district.

Urban particulate matter (PM) was collected with a high-volume sampler (MCV, Model CAV-A/HF, Barcelona, Spain) [21], equipped with a five-stage standard cascade impactor, plus a back-up filter (MCV, Model IC/CAV, Barcelona, Spain) [22]. Different stages of cut-off points at 50% efficiency were the following equivalent aerodynamic diameters (D_p): stage 1, >10 μm; stage 2, 10-4.9 μm, stage 3, 4.9-2.7 μm, stage 4, 2.7-1.3 μm, stage 5, 1.3-0.6 μm and stage 6, <0.6 (0.6-0.01) μm. Granulometric fractions are in accordance with the particle size fraction definitions for health-related sampling [23]. Micro-fibre quartz filters were used for collection (WHATMAN, QM/A). Glass fibber filters were used in our previous works but they contain higher metallic content than quartz filters, and some elements cannot be measured. The quartz filter allowed for the determination of various metals not discernible with the glass filters, such as sodium, potassium, aluminium, zinc, chromium and barium. The only negative factor of quartz filters is always the high cost.

A high number of samples are necessary for complete information. Eighty-three samples were collected every four days during twelve months. So, weekly samples were usually taken on different days each week, obtaining samples of every day of the week. Sampling periods were from 0:00 a.m. to 23:59 p.m.

Before the analysis of samples, filters used for dust collection size were previously dried in a desiccator for a 48-h period in a dark room and weighed in an analytical balance according to the international recommendation [24]. Care was taken in handling the quartz filters in order to avoid contamination problems and all filter materials and samples were handled within a vertical laminar airflow cabinet (INDELAB with HEPA filter, Model IDL-48V), for ensuring air cleanliness standards of class 100 according to Federal Standard 209E [25].

Reagents and apparatus

A water bath (JULABO, Model SW-20C) with temperature controlled for heating the samples was used. Acid digestions and extractions were carried out in polypropylene centrifugal tubes HEBOLAB. Centrifugations were performed at 5000 r.p.m. for 10 min (SIGMA, Model 3-15). All reagents and standard solutions were from MERCK and the milli-Q-grade water was from WATERS-MILLIPORE (Model Plus). Metallic extractions of the chemical speciation scheme were carried out in a rotator at room temperature.

Metal concentrations of more than twenty elements were analysed by inductively coupled plasma atomic emission spectrometry (ICP-AES) using a Fisons-ARL 3410 sequential multi-element instrument. The results presented in the current work were focused mainly on the heavy metals Pb, Ni and Cd recommended by the Framework and the Fourth Daughter Directives. Other inorganic (Hg and As) and organic compounds (PAHs) were determined in other campaign recently finished. Wavelengths were chosen in order to avoid possible interference of elements from the analytical determinations. Analyses of acid solutions on ICP-AES showed sample viscosity importance, so calibration graphs were prepared in the same acid matrix as the samples.

Methodology for the chemical analysis

For the metal concentrations each filter was digested with a mixture of nitric, hydrochloric and perchloric acids (6:2:5) in centrifugal tubes at 95°C for 90 min in water bath. This mixture was optimised between other two bi-acid mixtures, nitric-perchloric and nitric-hydrochloric, giving the best results. A set of unexposed filters was analysed as blanks using the same procedure used for samples. This method is similar to the reference method ISO 9855 [26] for analysis of lead recommended in the 99/30/EC Daughter Directive. But the Proposal for the Fourth Daughter Directive also recommends the use of ICP detection and other digestion acid mixtures equally valid.

The size distribution of metals (physical speciation) is the metal concentration in each size fraction according to the impactor specifications mentioned above. The nomenclature consisted in using the symbol of the element plus a number from 1 to 6. For example, Pb6 represents the lead associated with particles below 0.6 micrometers; Cd2 represents cadmium associated with particles between 10 and 4.9 micrometers. For total metal concentrations, that is, the sum of stages 1 to 6, the nomenclature is PbT and CdT.

On the other hand, chemical speciation of metals in fine particles was determined by applying the sequential extraction scheme shown in Table 1. The sequential procedure was described in [27]. In this case the nomenclature consisted in using the symbol of the element plus the number 6 (finest particles) and a letter from A to D.

Statistical analyses

The results of the analytic measurements were numerous, from more than eighty samples, and some of these variables can possibly be related to each other. To relate many variables, the analysis of correlations has been used in all previous works. The Pearson Product-Moment correlation have then been studied by applying the CSS:STATISTICA (StatSoft) software package. The interpretation of the correlation results consist 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 one metal increases their concentration in the air, parallelly to other metal through different sampling sites and different days, one can consider that these metals come from the same emission source. 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 (outliers) 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. This way many high correlation coefficients were discarded. Also many eclipsed valid correlations, that initially had low correlation coefficients, were discover with high correlation coefficients when these outliers were removed.

Results and discussion

Particles and gas pollutants

High amounts of particles were collected at this traffic site. An average of 96.7 µg m^{-3} for TSP

with maximums and minimums around 170 and 47 μg m^{-3} were obtained. The typical bimodal distribution obtained was: one, a fine mode below 0.6 μm aed (for the backup, 46%), and the other was a coarse mode up to 4.9 μm aed (on stage 1 and 2, 37%). The results show the importance of preferential by studying fine particles. The range of TSP collected covers from fine particles of around 0.01 micrometers to about 30-50 micrometers. Therefore, particles lower than 10 micrometers (PM10) represent 80% (77.3 μg m^{-3}) of the Total Suspended Particles. In addition, this concentration exceeds the annual limit value of PM10 for the protection of human health (40 μg m^{-3} for 2005, 20 μg m^{-3} for 2010). Also, many values have exceeded the daily limit value for PM10 (50 μg m^{-3}), exceeding it 72 out of 83 samples (87%), more than the permitted 35 annual exceedances (about 10%) that the directive will accept until 2005 (7 annual exceedances until 2010). The majority of these values represent a daily air quality index of 'bad air quality'.

However particles lower than 1 μm (PM1) and 2.5 μm (PM2.5) represent 51% and 56% of the total particles. This fact is one of the aspects that leads actually to the study of only PM10 using a reference method of sampling in the international community. The European regulatory laws will soon create mandatory measurements on PM2.5, as in other countries around the world.

In relation to gas pollutants, the annual mean values were 50.5 μg m^{-3} for NO_2 and 10.4 μg m^{-3} for SO_2. Limit values are 40 μg m^{-3} for NO_2 (annual average) and 20 μg m^{-3} for SO_2 (annual average). Therefore the annual average value obtained in the Ranilla automatic gauge was higher than the limit value for NO_2 and lower for SO_2, approximately half the EU value.

Physical speciation of heavy metals

Physical speciation of lead showed the highest concentration in the finest particles (Pb6, 57 %); meanwhile, lead in coarse particles (Pb1+Pb2) was only 18 % (Fig. 1-c). This figure represents the mean profile found for a traffic source for air concentration units. However, the profile is completely different if the data are expressed as mass concentration units (mg Kg^{-1}). In this case, the highest concentrations of lead were distributed in a mode between 4.9 and 0.01 μm (Pb3 to Pb6, 86 %), where lead between 2.7 and 0.6 μm represented 51 % (Pb4+Pb5) and lead in particles under 0.6 μm (Pb6) represented only 18 %; meanwhile, lead in coarse particles was 14% (Pb1+Pb2). This is an opposite profile from that found in air concentration units. The interpretation of this fact is important because it implies that the high air concentrations of lead found in particles lower than 0.6 μm are due to the highest abundance of this fine size mode in the atmosphere. However, the high mass concentrations of lead found in particles between 2.7 and 0.6 μm are due to the high enrichment in metal contents of this size range, mainly particles between 2.7 and 1.3 μm (Pb4, 27 %). Therefore, these particles are those most directly related to the lead emissions and one can assume that they could be better considered as markers, in metallic richness units, for traffic sources rather than the finest particles (< 0.6 μm).

For cadmium and nickel metals, the physical speciation in air concentrations showed the same distribution (Fig. 1-a and 1-b). These profiles were different to those of lead because concentrations in particles under 0.6 μm reached only 45% for nickel and 39% for cadmium. Therefore the harmful physical and chemical effects on lungs are less in these metals with regard to the highest percentages of lead (57%). However, the physical speciation in mass concentration was different comparing nickel and cadmium. The profile for cadmium was similar to that of lead. The difference was found in the nickel profile when metallic richness increases in particles between 4.9 and 2.7 μm (Ni3) and decreases in particles between 2.7 and 1.3 μm (Ni4). Therefore, both metals most likely originate from different sources, constituting further evidence of source differences, as was mentioned above, where cadmium probably has a similar origin as lead, the traffic.

On the other hand, the size distribution allows characterisation of the PM cut-points at 10, 2.5 and 1 micrometers. The relation to lead shown in Table 2 indicates the highest contribution of PM10 to TSP (0.93) regarding nickel and cadmium (0.84 and 0.79). This high contribution is valid also for the contribution of PM2.5 to PM10 (0.79, 0.66 and 0.53) but not for PM1 to PM2.5 which were similar (0.88, 0.86 and 0.80). This fact leads to the same consequence mentioned above concerning the advisable future reduction in the size cut-point in the PM-inlet of samplers. These ratios recommend that PM1 particles should be the next objectives, after the method for sampling PM2.5 is normalised.

Lead and relationship with traffic, gases and meteorology

The average lead concentration in the 'Ranilla' automatic gauge was 249 ng m^{-3}, below the limit value of 500 ng m^{-3} given in the EU-Directive 99/30/EC. This maximum value was reached for only a few days. This limit value was surpassed in some industrial sites of Seville, such as foundries [28]. However, the daily emission of this heavy metal from traffic represents a more serious risk for human health than only a few days per year near a foundry. Actually, lead emissions from cars in Spain has not existed since 15th December 1999 when leaded gasoline was no longer sold, according to the EU recommendations. Only industrial emissions throw out lead, or resuspended particles containing accumulated lead in the soil blown into the air by wind and/or traffic or farming movement [29]. Additionally, lead from gasoline breathed by citizens before this date can still be in their bodies.

Nevertheless, in 1997-1998 lead emissions from general traffic were already lower than previous years because of the EU mandate that new vehicles have to be manufactured with a catalyssator starting in 1990. Usually lead concentrations in Seville's air before 1990 were around 1.5 µg m^{-3} [30]. Besides, about this time, lead in gasoline was reduced from its content of 4.0 to 0.15 g l^{-1} and unleaded gasoline contained a maximum of 0.0013 g l^{-1}. But in 1997-1998 the automotive park consisted of a majority of old cars, consequently, important leaded exhausts were still being emitted.

The weekly variation of lead air concentrations shows that lead emissions were higher on weekdays (251 ng m^{-3}) than at weekends (207 ng m^{-3}), as the traffic varied (Fig. 2). On Sundays lead emissions and traffic intensities were extremely high (273 ng m^{-3}). This was due to vehicles returning from weekend recreation. The weekly variation of lead mass concentrations did not show any differences between weekdays (2400 mg Kg^{-1}) and weekends (2360 mg Kg^{-1}); that is, the lead composition of particles was the same, the only difference being the amount of particles emitted by traffic.

The correlation of total lead concentrations with traffic intensities is shown in the seasonal variation (Fig. 3) where the traffic intensities are proportionally related to lead emissions. However the proportionality does not always have the same magnitude and consequently the correlation coefficient is low, r = 0.39 (Fig. 4-a). There is some excessive traffic intensity data (Fig. 3), attributed to errors caused by traffic jams. When one removes these outliers, which hide the real interrelation, correlation reaches the value r = 0.71 (Fig. 4-b). In relation to size distribution of lead, the size fractions most correlated with traffic intensities corresponded to lead associated with the fine particles under 4.9 µm (r = 0.68 for Pb6, r = 0.64 for Pb3, r = 0.58 for Pb2 and r = 0.66 for Pb4, Fig. 4-c). Correlation results of metallic richness were similar, the coefficient being higher than in inmission levels (r = 0.82 for PbT, r = 0.78 for Pb6, r = 0.74 for Pb4-Pb3 and r = 0.72 for Pb2). Fine particles are better correlated than coarse particles. Correlation coefficients in mass concentrations are higher than in air concentrations because the concept of metallic richness softens the effects of meteorological variables on the amount of particles in the air, mainly rain and winds.

Table 3 shows other parameters correlated with air concentrations of lead. These were the

gaseous pollutants from traffic, such as CO (r = 0.78) and NO_2 (r = 0.56). Lead associated with particles below 0.6 μm (Pb6) was again the correlated best with CO and NO_2 (r = 0.75 for CO and 0.54 for NO_2). The other size fractions of lead were also correlated with CO (r = 0.71 for Pb2, 0.68 for Pb1/Pb3) and with NO_2 (r = 0.52 for Pb1). Obviously, the correlation CO-NO_2 was high (r = 0.69), as well as the correlation between ozone concentrations and the solar radiation (r = 0.72), temperature (r = 0.65) and relative humidity (r = - 0.68).

In relation to other metals analysed, CO was also correlated with total barium concentrations (r = 0.63) the coarse size fraction (Ba1, r = 0.67) being the highest correlated, suggesting that this element also originated in traffic emissions [31-33]. Moreover, barium was highly correlated with lead (r = 0.83) as in other works [12], mainly in coarse particles, such as Pb2-Ba1 (r = 0.86), Pb2-Ba2 (r = 0.83) and Pb3-BaT (r = 0.76) pairs, as well as in finer particles, such as Pb4-Ba3 (r = 0.77), Pb4-BaT (r = 0.80), Pb4-Ba4 (r = 0.72) and Pb5-Ba4 (r = 0.68) pairs. Therefore, both fine and coarse particles were significant in relation to the traffic source, as the correlations Pb6-Ba1 (r = 0.73) or Pb4-Ba2 (r = 0.78) show. NO_2 was also correlated with barium (r = 0.59), mainly with the coarse fraction again (NO_2-Ba1, r = 0.55, NO_2-Ba2, r = 0.46). Lead was also correlated with copper. The correlation coefficient for total concentrations was represented by the pair PbT-CuT (r = 0.68). The highest coefficient for size fractions were for the Pb6-CuT (r = 0.67) pair, and for the Pb1-Cu1 (r = 0.81), Pb2-Cu2 (r = 0.79). The Pb-Cu pair indicate the origin of copper from brakes-lining in cars [34].

With respect to the relation to meteorological variables, the carbon monoxide level in air is highest at high values of relative humidity than at low values (r = 0.63). This correlation is found also for total lead (r = 0.70), Pb2 (r = 0.78) and Pb3 (r = 0.72). Probably lead aerosols become better in coarse particles when the air humidity increases. Furthermore, total lead concentrations decrease when wind speeds increase (r = - 0.48). The size fractions Pb3, Pb4 and Pb5 are those easiest removed by high wind speeds (r = - 0.62 for all them).

Other correlation results between size fractions of metals show that other correlations higher than 0.7 were obtained for Pb1, Pb2 and Pb3 with S1 (r = 0.78), Pb2 and Pb3 with S2 (r = 0.75), and Pb1 and Pb3 with Zn1 (r = 0.77).

Nickel and cadmium and their relationships

Nickel together with vanadium is usually from fuel oil. However, nickel has also been associated with vehicle emissions. Cadmium is also associated with motor traffic emissions as a constituent of motor alloys [35,29] or in electronic components and battery of cars. Due to cadmium impurities in zinc minerals, cadmium also accompanies zinc oxides used in tire manufacturing [31, 36].

The averages of nickel and cadmium concentrations were 6.9 and 1.0 ng m^{-3}, respectively. Both concentrations are above the Unit Risk (U.R.) values based on cancer of the WHO and EU guidelines, 2.5 ng m^{-3} for Ni and 0.24 ng m^{-3} for Cd. However, both are lower than the non-cancer limit values of the Proposal for the Daughter Directive presented by the European Commission (20 ng m^{-3} and 5 ng m^{-3}).

The weekly variation of air levels shows that nickel concentrations predominate only during weekdays, decreasing on Saturdays and Sundays. Cadmium has a similar variation (Fig. 5). However, the weekly variation of metallic richness shows a high decrease at the weekends with regard to the weekdays for nickel and there isn't a decrease for cadmium. These results show that cadmium has the nearest behaviour to that of lead, indicating that it could originate from traffic. Therefore, nickel most probably originates from industrial sources. The decrease of nickel suggests the decrease of industrial activities at the weekends. This different origin was confirmed because correlation between the two metals did not show any relationship. At the Ranilla traffic site the industrial source probably comes from the industries that line both sides

of the Highway, carried out on the wind that flows down the road like the traffic.

In relation to the correlation analysis, no clear correlation was observed between nickel, cadmium and lead. Also, no direct relationship was observed for nickel and cadmium with the gaseous pollutants CO and NO_2. Correlations between nickel and other elements, such as nickel-vanadium (r = 0.70) and nickel-sulphur (r = 0.57) were found, indicating the usual content of nickel-vanadium in industrial fuels. The best correlations for NiT-VT and NiT-ST pairs were found for fine fractions, the Ni6-V6 pair (r = 0.72) and the Ni6-S6 pair (r = 0.57). These results showed that Ni, V and S in fine particles originated from fuel combustion at near by industries. Correlations found between cadmium and other elements were cadmium-manganese (r = 0.71), cadmium-zinc (r = 0.60) and cadmium-iron (r = 0.58). These correlations were found by other authors as a traffic source [31] and they constitute other evidence of the traffic origin mentioned above. In relation to the size distribution, the best correlations for the CdT-MnT, CdT-ZnT and CdT-FeT pairs were found for coarse and fine particles, Cd2-Mn2 (r = 0.73), Cd3-MnT (r = 0.74), Cd5-Zn4 (r = 0.66), Cd5-Zn5 (r = 0.67), Cd2-Fe2 (r = 0.62) and Cd3-Fe3 (r = 0.62).

In brief, lead and cadmium came from traffic and they were both associated with fine and coarse particles. Nickel, vanadium and sulphur came from industries and were associated with fine particles. The relation to the relative humidity was found to be clearer for lead, and this fact explained the presence of both fine and coarse particles in aerosols that came from traffic.

Chemical speciation of metals in fine particles

The characterisation of heavy metals by chemical speciation is actually the best way to relate the presence of toxic metals in the air along with their harmful effects on human health [37]. The relation between the levels of chemical forms in particles and their bioavailabilities through the respiratory tract is the differentiating characteristic regarding the level of total metal concentrations.

The results presented in Table 4 show the high concentration of the most bioavailable chemical forms of nickel (31%). Cadmium is also notably present in the air in this soluble fraction (20.5%). Fortunately, lead has a low presence in soluble chemical forms (3.5%); however, the presence of lead in the fraction of reducible compounds (35%) is significant. Cadmium also contributes to this second fraction, consequently being the heavy metal whose chemical compounds correspond to the two most bioavailable fractions (52%). In relation to the third fraction of metals bound to organic matter and/or sulphides, the high presence in nickel and lead demonstrates the relationship to the fuel combustion from industries or vehicles. Cadmium also presents a considerable percentage of these types of chemical forms. The two most abundant chemical fractions in each metal correspond to fractions A and C for nickel, representing 75% of the total and fractions B and C for lead (84%) and for cadmium (60%). Residual chemical forms are practically not bioavailable for human lungs.

Studying the weekly variation of the most harmful chemical forms one observes that the Pb6A forms predominate at the weekends, like the Cd6A ones, meanwhile the Ni6A forms predominate on weekdays. This is a negative factor since people spend more time outside their homes at the weekends. However, the reducible chemical forms of the three heavy metals predominate more on weekdays than at the weekends.

Correlation studies show clear correlations between the most abundant chemical forms of lead, Pb6B and Pb6C, and traffic variables, such as NO_2 (r = 0.55 and 0.57), CO (r = 0.67), BaT (r = 0.57) and CuT (r = 0.63). Other correlations found were Pb6C-Cu6C (r = 0.61), Pb6B-Cu6B (r = 0.54) and Pb6D-Cu6D (r = 0.53), which indicate the chemical composition of metals related to brake-lining emissions of cars.

The correlations for nickel were Ni6A with SO_2 (r = 0.56), Ni6A-Ni6B with ST (r = 0.57-

0.54) and VT (r = 0.77-0.69), which indicate the chemical forms associated with nickel contained in solid and liquid fuels. Correlations found for S and V chemical fractions were Ni6A-V6A (0.87), Ni6A-V6B (0.82), Ni6B-V6B (0.74), Ni6B-V6A (0.66), Ni6C-V6C (0.72), Ni6D-V6D (0.73), Ni6A-S6A (0.60), Ni6A-S6B (0.58).

Finally, only a few correlations were found for cadmium speciated forms, such as Cd6B-MnT (0.55), Cd6B-ZnT (r = 0.53), Cd6B-Zn6B (0.72), Cd6B-Cu6A (0.75) and Cd6B-Mn6A (0.59).

The importance of the results of speciation is vital because one can find out what types of chemical compounds are associated with specific sources, together with the information about potential toxicity and bioavailability to the population.

Conclusions

A large period of sampling with many samples collected in different situations has demonstrated be necessary to obtain a sufficient and rich analytical and environmental information. The use of ultrapure quartz filters has been vital to determine trace metal concentrations, such as barium or zinc. The characterisation of a traffic site by physical speciation in air concentrations revealed that the degree of accumulation of lead in the finest particles, less than 0.6 μm (57%), was higher than in nickel (45%) and cadmium (39%). Besides, physical speciation in mass concentrations (metallic richness) showed that accumulation of lead in the size range between 2.7-0.6 μm (51%), was also higher than in nickel (40%) and cadmium (44%). Therefore, lead is the pollutant more concentrated in fine particles less than 2.7 μm. The high concentrations of particles and metals found in fine particles less than 0.6 μm in air concentrations was the reason to study the chemical speciation on these finest particles. In this sense, nickel constituted the heavy metal more harmful because of the high solubility of its chemical forms presented in air samples. Fortunately the contrary result was obtained for the heavy metal more abundant, the lead metal. However, one have to keep in mind that lead is the element more presented in the second and third fractions (oxidisable and organic matter-sulphides forms) in 84%, chemical forms also potentially bioavailables, and that it was presented in the no bioavailable forms (fourth fraction, residual) only in 12%.

Various similarities were found between cadmium and lead in this traffic site: the weekly variation of total air levels showed that cadmium had the same profile to that of lead, indicating that it could also originate from traffic. Their physical speciation showed that both fine and coarse particles were correlated as in the case of lead, probably due to the effect of the air humidity. Besides, the profile of physical speciation of cadmium was similar to that of lead. In addition, the weekly variation of the soluble chemical forms of lead and cadmium in the finest particles showed that they predominated at the weekends, contrarily to the nickel. So, several evidences lead to the conclusion that one can assert a traffic origin of cadmium in high trafficked sites of a large city. Analytical data of physical and chemical speciation and correlation studies assigned a clear industrial origin of nickel.

The search for a tracer element that substitutes the metal lead when leaded gasoline not exists lead us to find the metals copper and mainly barium as those clearly originated from traffic emissions. Besides, both metals are sufficiently detectable in the urban air. Clear relationships between the barium and copper metals with total lead concentrations, its physical and chemical speciation and with gaseous pollutants demonstrated this relationship with vehicular emissions. Other cities more industrialised has important emissions from various types of industries (big foundries, steel factories or chemical and pharmaceutical industries). Therefore, only barium have to be the metal proposed as tracer of traffic pollution when the industrial influence is low in a city, like in Seville.

Finally, the use, design and reference method of PM1 inlets is proposed as the best sampling system for airborne fine particles in relation to the harmful health effects produced by heavy metals.

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Captions to the figures

Fig. 1 Physical speciation of cadmium (a), nickel (b) and lead (c). These size distributions are expressed as percentage of the sum of the six stages. Continuous lines represent the average profile of the percentages obtained from the metallic richness (mass concentration) in mg Kg^{-1}. Discontinuous lines represent the profile of the percentages obtained from the inmission level (air concentration) in ng m^{-3}.

Fig. 2 Average weekly variations from Mondays to Sundays of traffic intensities and total lead concentrations during the sampling period. Differences between weekdays and weekends are also shown. Lead concentrations are represented in air and mass concentrations.

Fig. 3 Seasonal variation of traffic intensities and total lead concentrations in urban air during all sampling period (83 samples collected). A clear parallelism or correlation is shown by the lead emissions when the traffic intensities increase and decrease sequentially.

Fig. 4 Graphic representation of the correlation between traffic and total lead when outliers are present (a). The visual correlation is better distinguished when outliers were removed (b). Representation of the size fraction of lead best correlated with traffic (Pb4) is also shown (c).

Fig. 5 Average weekly variations of traffic intensities and total nickel and cadmium concentrations. Metal concentrations are also represented in air and mass concentrations.

Table 1 Size distribution of the metals (physical speciation)

Stage/fraction	1	2	3	4	5	6
Range aed (μm)	> 10	10–4.9	4.9–2.7	2.7–1.3	1.3–0.6	< 0.6
Physical speciation	DTSP/ FM					
Sum of fractions	TSP					
		PM10				
				PM2.5		
					PM1	
Chemical speciation						PM0.6/SM

Table 2 Speciation scheme applied according to Fernández-Espinosa et al. (2001)

Metallic species	Reagent	Experimental conditions
A. Soluble and exchangeable: extremely bioavailable	15 ml H_2O (pH=/.4)	3 h. at room temperature. Shaker agitation
B. Carbonates and oxides: bioavailable	10 ml NH_2OH•ClH 0.25 M at pH =2	5 h. at room temperature. Shaker agitation
C. Bound to organic matter: bioavailable	7.5 ml H_2O_2 30% + 7.5 ml H_2O_2 30% + 15 ml NH_4AcO 2.5 M at pH =3	at 95°C until near dryness Shaker agitation + a 95°C until near dryness Shaker agitation + 90 min. at room temperature. Shaker agitation
D. Residual: not bioavailable	10 ml (HNO_3 : HCl : $HClO_4$) (6 : 2 : 5)	5 h. at 95°C Shaker agitation

Table 3 Ratios between TSP, PM10, PM2.5 and PM1 particles obtained from impactor data

	PM10/TSP	PM2.5/PM10	PM1/PM2.5	Mean
Particles	0.80	0.69	0.91	0.80
Lead	0.93	0.79	0.88	0.87
Nickel	0.84	0.70	0.88	0.81
Cadmium	0.81	0.67	0.83	0.77
Barium	0.69	0.39	0.78	0.62
Copper	0.79	0.48	0.77	0.68
sulfur	0.90	0.81	0.89	0.87
Vanadium	0.87	0.76	0.91	0.85
Iron	0.72	0.47	0.80	0.66
Zinc	0.84	0.66	0.78	0.76
Manganese	0.75	0.56	0.83	0.71

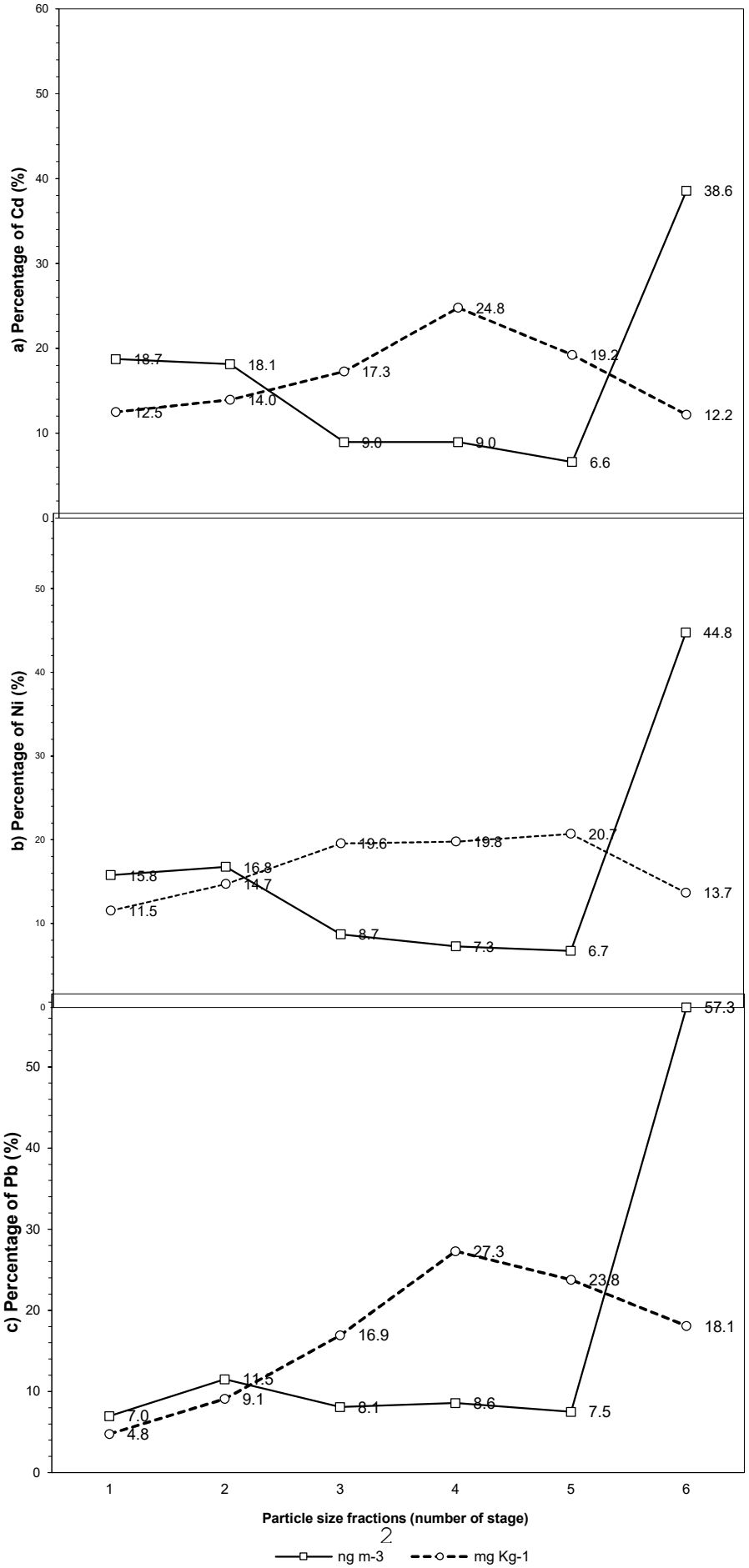
Table 4 Correlation matrix formed by the variables total suspended particles, gas pollutants, meteorological variables, total metals and physical size fractions of lead.

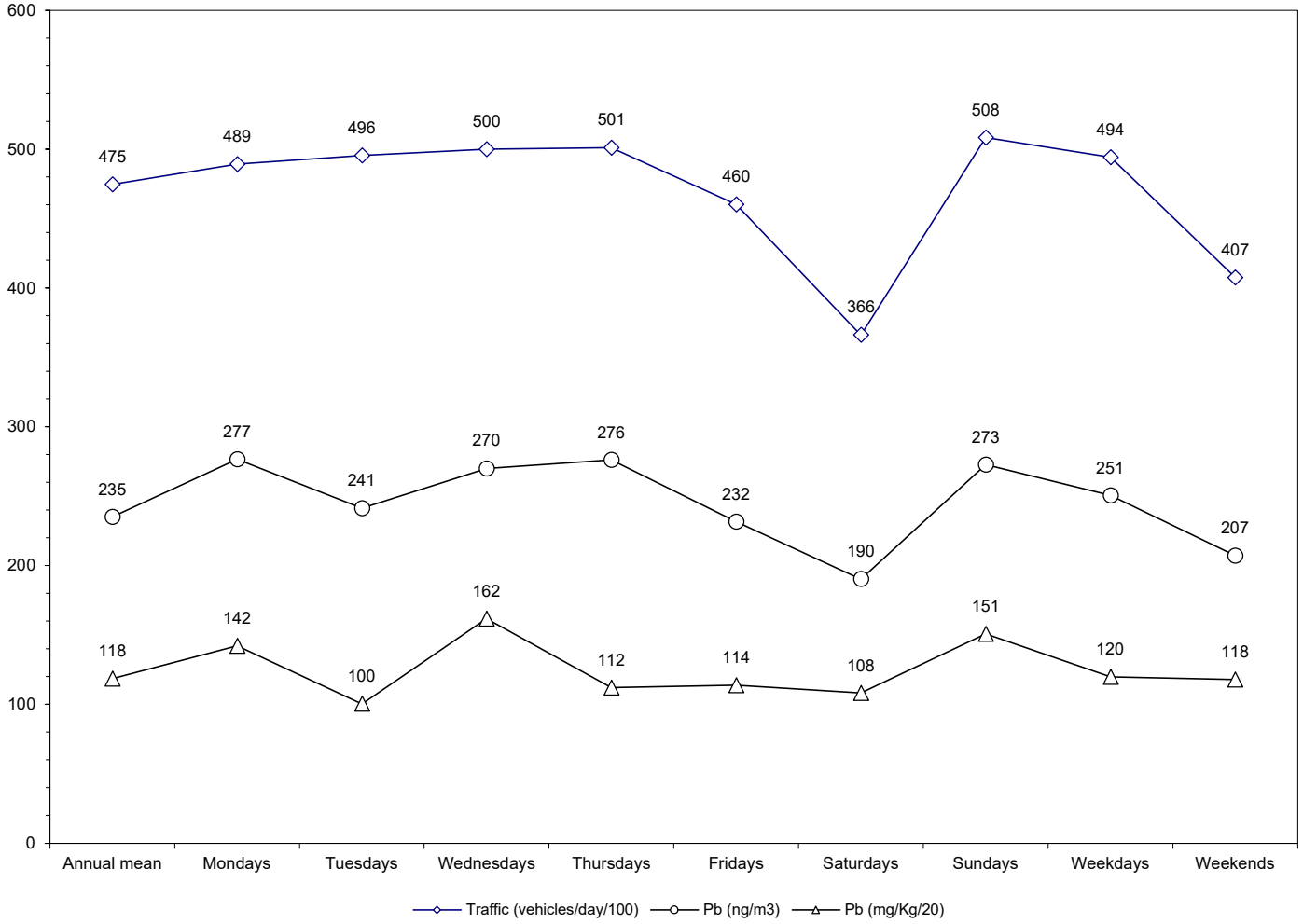
	TSP	SO_2	NO_2	O_3	CO	TR	WS	AT	AP	RH	SR	S	Fe	Pb	Zn	Cu	Ba	Mn	V	Ni	Cd	Pb1	Pb2	Pb3	Pb4	Pb5	Pb6
TSP	1.00																										
SO_2	0.25	1.00																									
NO_2	0.19	0.37	1.00																								
O_3	-0.01	0.07	0.06	1.00																							
CO	-0.08	0.22	0.69	-0.06	1.00																						
TR	0.31	0.34	0.46	-0.08	0.59	1.00																					
WS	-0.26	-0.03	-0.08	0.02	-0.02	-0.17	1.00																				
AT	0.17	0.39	-0.06	0.65	-0.38	-0.17	0.31	1.00																			
AP	0.34	-0.26	-0.06	0.13	-0.02	0.02	-0.63	-0.34	1.00																		
RH	-0.39	-0.18	0.14	-0.68	0.63	0.28	-0.10	-0.72	-0.03	1.00																	
SR	0.15	0.31	-0.09	0.72	-0.37	-0.23	0.30	0.74	-0.19	-0.82	1.00																
S	0.52	0.26	0.12	-0.06	0.03	0.27	-0.05	0.26	-0.05	-0.14	0.19	1.00															
Fe	0.91	0.27	0.26	0.06	-0.06	0.28	-0.40	0.11	0.35	-0.37	0.15	0.44	1.00														
Pb	0.13	0.30	0.56	-0.01	0.78	0.71	-0.48	-0.42	0.03	0.70	-0.36	0.11	0.17	1.00													
Zn	0.38	0.35	0.14	-0.05	0.13	0.38	-0.42	0.14	0.06	-0.11	0.14	0.35	0.47	0.35	1.00												
Cu	0.23	0.38	0.32	-0.19	0.44	0.27	-0.38	-0.14	-0.02	0.31	-0.37	0.21	0.36	0.68	0.49	1.00											
Ba	0.22	0.28	0.59	-0.06	0.63	0.52	-0.37	-0.37	0.03	0.42	-0.38	0.09	0.37	0.83	0.40	0.73	1.00										
Mn	0.79	0.39	0.20	-0.04	-0.08	0.25	-0.41	0.21	0.20	-0.33	0.15	0.46	0.89	0.13	0.68	0.42	0.42	1.00									
V	0.61	0.57	0.16	-0.07	-0.03	0.36	-0.26	0.30	-0.06	-0.24	0.21	0.73	0.62	0.19	0.56	0.34	0.25	0.69	1.00								
Ni	0.34	0.43	-0.03	-0.07	-0.11	0.07	-0.05	0.39	-0.18	-0.30	0.34	0.66	0.35	0.00	0.46	0.21	0.03	0.50	0.72	1.00							
Cd	0.41	0.09	0.02	-0.01	-0.08	0.10	-0.25	0.11	0.20	-0.22	0.19	0.32	0.58	0.04	0.60	0.41	0.01	0.71	0.31	0.34	1.00						
Pb1	0.15	0.13	0.52	-0.08	0.68	0.53	-0.23	-0.48	0.14	0.56	-0.44	0.24	0.16	0.80	0.27	0.55	0.76	0.13	0.20	-0.01	0.07	1.00					
Pb2	0.04	0.04	0.46	-0.10	0.71	0.58	-0.32	-0.64	0.13	0.78	-0.59	0.06	0.10	0.88	0.25	0.56	0.74	0.06	0.06	-0.18	-0.04	0.84	1.00				
Pb3	0.15	0.11	0.46	-0.12	0.68	0.66	-0.35	-0.56	0.17	0.72	-0.45	0.13	0.22	0.88	0.42	0.61	0.82	0.18	0.16	-0.05	0.09	0.72	0.86	1.00			
Pb4	0.24	0.16	0.47	-0.02	0.65	0.68	-0.43	-0.53	0.23	0.43	-0.40	0.11	0.31	0.90	0.47	0.63	0.80	0.26	0.20	-0.03	0.11	0.71	0.86	0.94	1.00		
Pb5	0.36	0.15	0.44	0.15	0.49	0.60	-0.49	-0.41	0.27	0.22	-0.27	0.18	0.45	0.79	0.53	0.56	0.71	0.38	0.30	0.04	0.13	0.61	0.73	0.79	0.88	1.00	
Pb6	0.06	0.42	0.54	0.03	0.75	0.70	-0.09	-0.23	-0.12	0.39	-0.21	0.07	0.08	0.95	0.27	0.67	0.76	0.05	0.18	0.05	0.02	0.67	0.72	0.73	0.75	0.63	1.00

TR is traffic intensity. Meteorological data are represented by wind speed (WS), ambient temperature (AT), atmospheric pressure (AP), relative humidity (RH) and solar radiation (SR).

Table 4 Results of air concentration and percentages obtained in the different fractions of chemical speciation

Fraction	A	B	C	D
Metal	Air concentration (ng m^{-3})			
Lead	5.0	49.3	71.2	17.0
Nickel	0.95	0.34	1.37	0.43
Cadmium	0.079	0.121	0.111	0.075
Barium	0.08	2.69	3.08	0.42
Copper	1.58	1.36	5.27	1.95
sulfur	786.3	348.3	163.4	41.5
Vanadium	1.66	1.06	1.11	0.41
Iron	1.5	19.2	140.3	148.7
Zinc	14.4	10.5	13.5	1.3
Manganese	2.42	1.65	2.54	1.21
	Percentage			
Lead	3.5	34.6	49.9	12.0
Nickel	30.9	11.0	44.2	13.8
Cadmium	20.5	31.3	28.8	19.5
Barium	1.2	42.9	49.2	6.7
Copper	15.6	13.4	51.9	19.0
sulfur	58.7	26.0	12.2	3.0
Vanadium	39.2	24.9	26.1	9.8
Iron	0.5	6.2	45.3	48.0
Zinc	36.3	26.4	34.0	3.2
Manganese	31.0	21.1	32.5	15.4


a) Percentage of Cd (%)
18.7
18.1
9.0
9.0
9.0
6.6
38.6
12.5
14.0
17.3
24.8
19.2
12.2
b) Percentage of Ni (%)
15.8
16.8
8.7
7.3
6.7
44.8
11.5
14.7
19.6
19.8
20.7
13.7
c) Percentage of Pb (%)
7.0
11.5
8.1
8.6
7.5
57.3
4.8
9.1
16.9
27.3
23.8
18.1
Particle size fractions (number of stage)
ng m-3
mg Kg-1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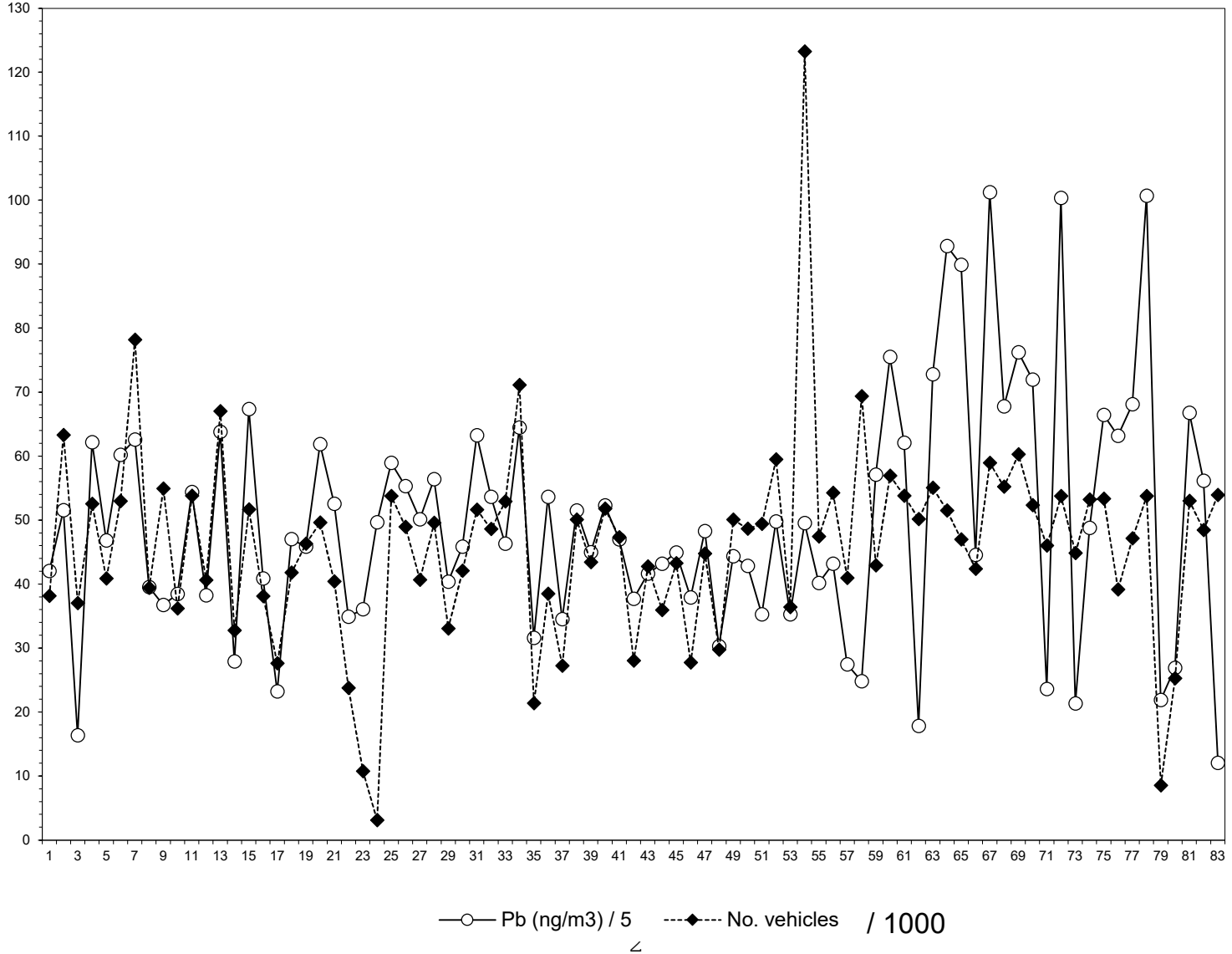
276
232
190
273
251
207
118
142
100
162
112
114
108
151
120
118
Annual mean
Mondays
Tuesdays
Wednesdays
Thursdays
Fridays
Saturdays
Sundays
Weekdays
Weekends
Traffic (vehicles/day/100)
Pb (ng/m3)
Pb (mg/Kg/20)

Fig. 2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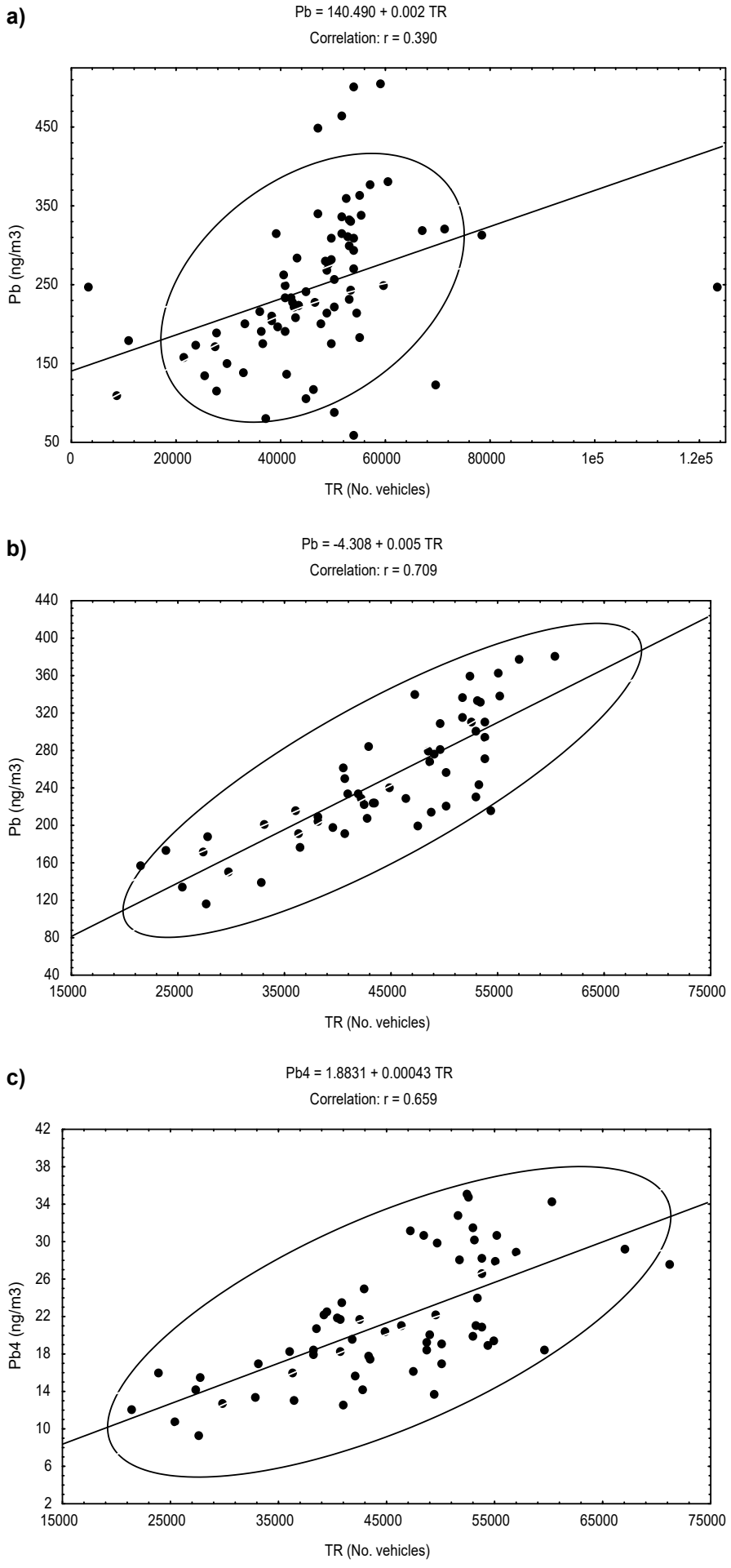
Pb (ng/m3) / 5
No. vehicles / 1000

Fig 4


a)
Pb = 140.490 + 0.002 TR
Correlation: r = 0.390
Pb (ng/m3)
TR (No. vehicles)
b)
Pb = -4.308 + 0.005 TR
Correlation: r = 0.709
Pb (ng/m3)
TR (No. vehicles)
c)
Pb4 = 1.8831 + 0.00043 TR
Correlation: r = 0.659
Pb4 (ng/m3)
TR (No. vehicles)

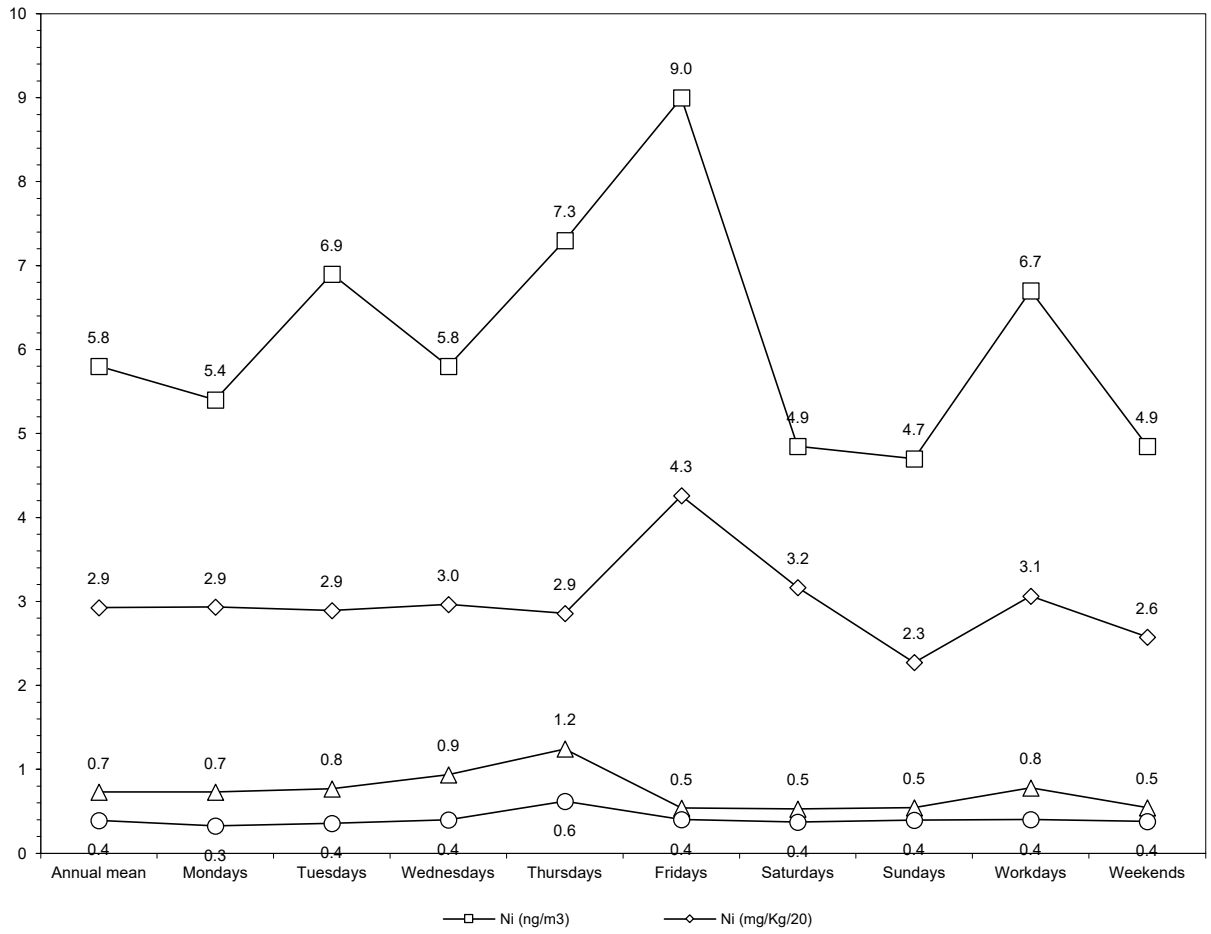

10
9
8
7
6
5
4
3
2
1
0
5.8
5.4
6.9
5.8
7.3
9.0
4.9
4.7
6.7
4.9
2.9
2.9
2.9
3.0
2.9
4.3
3.2
2.3
3.1
2.6
0.7
0.7
0.8
0.9
1.2
0.5
0.5
0.5
0.8
0.5
0.4
0.3
0.4
0.4
0.6
0.4
0.4
0.4
0.4
0.4
Annual mean
Mondays
Tuesdays
Wednesdays
Thursdays
Fridays
Saturdays
Sundays
Workdays
Weekends
Ni (ng/m3)
Ni (mg/Kg/20)

Fig. 5