

# **Influence of rain and other meteorological parameters on trace metals in size fractionated particles in polluted urban atmosphere**

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**Abstract**—Relationships between meteorological variables and particles, metals and their size fraction concentrations were determined from samples collected in different climatic situations. Special attention was focused on the effect of rain. Single correlation and multiple regression statistical methods were performed on samples from both rainy and dry days. Coarse particle concentrations diminished linearly when rainfall increased. The metals Fe, V, Ni, Ti, and Mn diminished as well. A substantial concentration effect was produced by the temperature on TSP, Fe, Ti, and Mn concentrations in fine particles. Also, a dispersion effect was produced by the atmospheric pressure on TSP, Mn, Fe, Ti, Ni, and V concentrations in these particles. Besides, there was a dispersion effect by the wind speed on TSP and Cd concentrations. The fine particles and metals between 1.3 and 0.6 micrometers are those best correlated with meteorological parameters. Multiple linear regression was demonstrated to be a powerful tool to explain the particle and metal levels in relation to size distribution and meteorology.

*Key-words:* size distribution, metals, suspended particles, meteorology, rain, multiple linear regression.

## ***1. Introduction***

Suspended atmospheric particles have long lifetimes depending on size and meteorological conditions. Size distribution depends on aerosol sources, but it is also affected by prevailing meteorological conditions. Apart from additional factors, meteorology is the most determinant factor in the removal or dispersion mechanisms of particles and metals in the air. Many studies have investigated the relationship between meteorological conditions and airborne particles (*Elsom and Chandler, 1978; Witz and Moore, 1981; Brooks and Salop, 1983*). The latter two used multiple linear regression analyses to relate meteorological parameters to particle and several metal concentrations in the USA, specifically in Los Angeles city and Southeastern Virginia State. We carried out a similar study on particles and lead in Seville (*Melgarejo et al., 1986*) using single and multiple correlations. The relation between meteorology and particle size distribution has also been the subject of numerous recent and

earlier works, such as *Choularton et al.* (1982) in Manchester (UK), *Väkevä et al.* (2000) in Helsinki, and *Despiau et al.* (1996) in a Mediterranean zone of France (Toulon), all of them using single correlations on particles.

To study the nature and magnitude of the meteorology effect on different particle sizes, the first tool is the statistical analysis of correlations (single linear regression). Thus, the first objective is to know, how meteorology influences different sizes, focusing specially on fine particles and toxic metals, which are the most harmful.

As a second important objective, multiple linear regression was considered as a statistical technique for the best information for particle and metal behavior caused by the meteorological parameters.

## ***2. Experimental section***

### *2.1 Measurement sites*

This study was done in Seville (38°12'–36°51'N, 4°39'–6°32'W, 10 m a.s.l.), the largest city in southern Spain. Analytical data were obtained from a network of twelve sampling stations already used in our previous works (*Usero et al.*, 1988; *Fernández et al.*, 1999 and 2000). The stations have different traffic intensities and different industrial activities, as well as zones with clean air. Seville is located in the centre of the Guadalquivir Valley, which opens toward the ocean at the base of the triangle that the valley forms.

The city has a warm and dry Mediterranean climate with mean annual temperature of 18°C, rainfall 600 mm, atmospheric pressure 1014 hPa, relative humidity 65%, and wind speed 2 m s<sup>-1</sup>. Seville is characterized by high temperatures and low wind speeds. Prevalent air currents come from the SW–NE direction. All these data are averaged from the 1961–1990 period (*MMA*, 1997). Predominant winds proceed from the Atlantic Ocean (southwest). Therefore, the situation of this sampling network in Seville represents the meteorological effects of a Mediterranean zone influenced by the African winds as in other cities of southern Europe.

### *2.2 Particulate sampling*

Atmospheric particles were collected with a high-volume sampler (MCV, Model CAV-A/HF) equipped with a five-stage cascade impactor plus a back-up filter (MCV, Model IC/CAV), which effectively separates the particles. It has the following equivalent cut-off diameters at 50% efficiency ( $D_p$ ): >10  $\mu\text{m}$  (A particles), 10–4.9  $\mu\text{m}$  (B particles), 4.9–2.7  $\mu\text{m}$  (C particles), 2.7–1.3  $\mu\text{m}$  (D

particles), 1.3–0.6  $\mu\text{m}$  (E particles), and  $<0.6 \mu\text{m}$  (backup, F particles). For A to E stages, five cut filters (14.2 cm  $\times$  14.2 cm) were used, and for the backup filter an uncut filter (20.3 cm  $\times$  25.4 cm) was used. Cut and uncut micro-fibre glass filters were purchased from WHATMAN (GF/A).

Granulometric fractions are in accordance with the particle size fraction definitions for health-related sampling (*ISO 7708*, 1995), which defines the fine particles as the fraction below 1  $\mu\text{m}$ . Thus, stages B to F can be associated with PM<sub>10</sub> particles, stages D to F with PM<sub>2.5</sub> particles, and stages E plus F with PM<sub>1</sub> particles (*Fernández et al.*, 2001). The flow rate should be set at the value of 68  $\text{m}^3 \text{h}^{-1}$  to get the size separation. The flow rate is calibrated every three months at the Andalusian Reference Laboratory for the Air Quality (LARCA) in Seville.

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, for ensuring air cleanliness standards of class 100 according to Federal Standard 209E.

Forty-one samples were collected in 1996, and three to four samples were usually taken at each sampling station. The sampling time-frame was usually 48 h (about 3264  $\text{m}^3$ ), and a weekly sample was taken on different days during the following week, so that a possible distorting effect could be avoided.

### *2.3 Reagents and apparatus*

Vertical laminar airflow cabinet with a HEPA filter was from INDELAB (Model IDL-48V). Water bath was from JULABO (Model SW-20C). Centrifuge was from SIGMA (Model 3-15). Standard solutions for metals and acids were from MERCK. Ultra-pure water was from WATERS-MILLIPORE (Milli-Q-grade, Model Plus).

Samples were analyzed for eleven metals (Ca, Fe, Mg, Pb, Cu, Mn, Ti, V, Ni, Co, Cd) by atomic emission spectrometry with inductively coupled plasma (ICP-AES) using a Fisons-ARL 3410 sequential multi-element instrument. Determinations in the multi-element analysis were done in triplicate for each sample.

### *2.4 Methodology for the chemical analysis*

Samples and blank filters used were stored, treated in a dark room and analyzed individually (A-F) for metal concentrations as in our previous work, *Fernández et al.* (2001). The particle concentration of each stage of suspended particles (FSP) was expressed in  $\mu\text{g m}^{-3}$ . The total suspended particles concen-

tration (TSP) was then calculated by summing the particle concentrations of the six fractions (FSP) of each sample.

The metal concentration of each filter (FM) was expressed in  $\text{ng m}^{-3}$ . The total metal concentration (TM) was then calculated by summing the concentration of the six fractions (FM) of each sample. To differentiate between the different size fractions, these were numbered from 1 to 6, e.g., Fe1 and Fe6 corresponded to the metal Fe collected in stages A and F, respectively.

## *2.5 Meteorological data*

Meteorological data were provided daily by our local service of the National Institute of Meteorology (INM) in Seville. These data correspond to the same periods of each particulate sampling. These values for each sampling correspond to the average hourly data provided throughout the sampling periods. Rainfall values were summed with the hourly data during the sampling period. The meteorological data are represented as follows: precipitation (PP) in mm, ambient temperature (AT) in  $^{\circ}\text{C}$ , atmospheric pressure (AP) in hPa, wind speed (WS) in  $\text{m s}^{-1}$ , and wind direction (WD) according to the cardinal points.

In this study we considered the rainy and dry days separately in two matrices, after dividing the “total matrix”, which showed some interesting results. The “dry days matrix” was formed by samples collected on non-rainy days, “rainy days matrix” was formed the by samples collected on rainy days.

## *2.6 Multivariate statistical analyses*

On the basis of the results, basic and multivariate statistical analyses were applied to the analytical and meteorological data. For these analyses the STATISTICA (*StatSoft*, 1999) software package was used.

Correlation studies were carried out by applying the simple linear regression (SLR) technique. 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 of choosing the highest correlation coefficients, but also verifying the linearity by 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 a graph, because their line is formed by accumulation of points at the extreme of their linear range and a lone point at the other extreme. In these cases, the correlation coefficients are due to only one sample and not all the experimental data. Outliers are misleading and should therefore be discarded.

Later on, multiple linear regression (MLR) analysis was used to relate the analytical variables, statistically significant in the SLR, to the meteorological parameters, through mathematical multivariate linear functions. For both SLR and MLR, when the correlation coefficient ( $r$ ) was not sufficiently high, a two-tailed t-test was applied with a 95% confidence level to assess whether  $r \neq 0$  was significant. Thus, if the calculated  $t$  of the student test was greater than the  $t$  tabulated, then  $r$  was significantly greater than zero.

From the first calculations of the data, we observed, that in Seville rain is the parameter with the greatest influence on particle and metal levels as opposed to the other parameters. The heterogeneity and distortion factor introduced by the washing effect of the rain makes the conclusions unreliable and justifies the need to treat each situation separately.

The statistical studies took into consideration, firstly, the effect of rain on total suspended particles and total metal concentrations and their size distributions, and secondly, the effect of the remaining meteorological parameters on particle and metal concentrations and their size distributions.

### ***3. Results and discussions***

#### *3.1 Meteorological characteristics of the sampling period*

During the whole year in 1996, a total of 916.8 mm of rainfall was registered, which represents a considerable increase compared to the previous years (580 mm in 1993, 327 mm in 1994, and 503 mm in 1995). Meteorological parameters recorded only for the sampling period are presented in *Table 1*. The mean rainfall on rainy days was 13.6 mm. Mean wind speed was low, 2.2 m s<sup>-1</sup>, although it was sufficient to cause the resuspension of soil particles in the air. Depending on maximum values, the effect can reach the dispersion of pollution. It should be noted also, that the temperatures were high. With regard to the frequency of the wind direction, the most common winds were south-westerly or southerly, although, the strongest winds came from the west (*Fig. 1-a*). This was to be expected, because the wind blows up the axis of the Guadalquivir Valley (SW–NE).

Table 1. Mean values of the analytical and meteorological variables corresponding to the sampling period

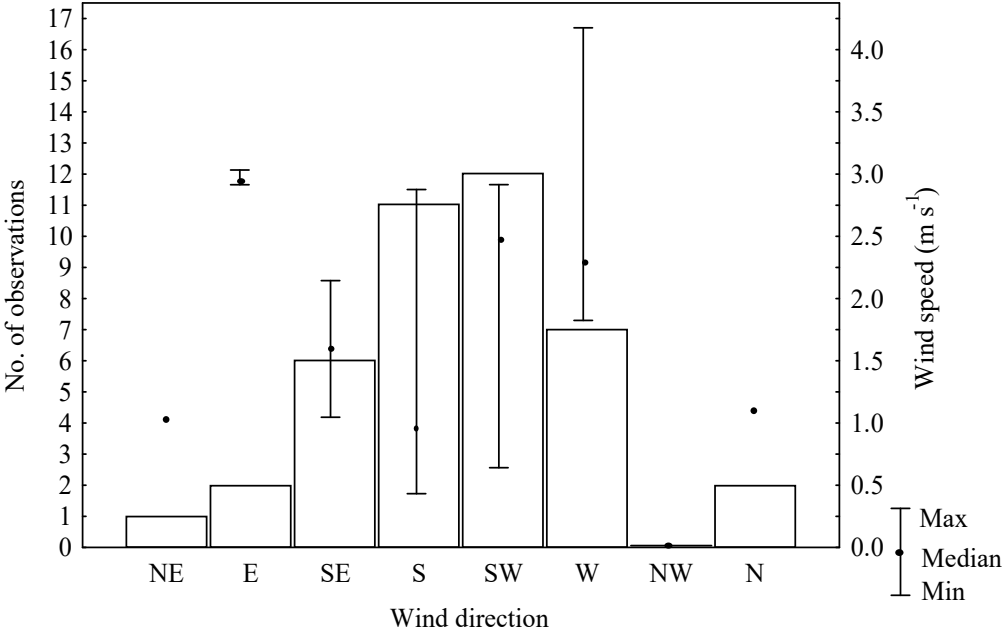
Variable	Mean	Range	Units	RSD (%)
<b>Meteorological variables</b>				
PP*	13.6	(1.2 – 141.0)	mm	167.8
WD	SW	(NW – W)		27.0
WS	2.2	(0.6 – 4.2)	m s <sup>-1</sup>	44.3
AT	21.0	(15.3 – 29.8)	°C	20.5
AP	1010.5	(1003.7 – 1018.4)	hPa	0.4
<b>Total and fractionated particle variables</b>				
TSP	78.7	(31.1 – 158.1)	µg m <sup>-3</sup>	44.0
A	12.1	(3.1 – 27.3)		53.6
B	12.4	(6.6 – 21.1)		33.4
C	4.9	(2.8 – 7.5)		26.9
D	4.0	(2.0 – 6.0)		31.2
E	3.6	(0.8 – 7.1)		46.4
F	41.7	(11.7 – 104.5)		57.0
<b>Total metal variables</b>				
Ca	2956	(345 – 8680)	ng m <sup>-3</sup>	81.6
Fe	689	(131 – 1974)		58.3
Mg	366	(200 – 669)		29.2
Pb	97	(15 – 1335)		60.0
Cu	28.0	(8.3 – 74.2)		51.5
Mn	19.8	(4.1 – 141.0)		52.6
Ti	7.4	(1.7 – 16.9)		52.0
V	5.9	(0.6 – 18.0)		76.5
Ni	1.97	(0.47 – 4.31)		58.9
Co	0.56	(0.09 – 2.01)		76.7
Cd	0.44	(0.09 – 4.73)		61.4

\*: Mean rainfall on rainy days, **RSD**: Relative standard deviation in percentage, **WD**: wind direction

The relationship between wind speed, rainfall, atmospheric pressure, and temperature is an important climatic feature. Thus, the correlation analysis is a good tool, because it shows meteorological behavior, for example, the well known relations between the rain, the decrease of temperature and atmospheric pressure, and the increase of wind speeds. Other results show that mild warm winds come from the south (proceeding from Africa) and slightly less warm winds from the Southwest (the Atlantic Ocean). The coldest winds are also the

strongest, those coming from the west (the Atlantic Ocean crossing Portugal). The highest rainfall values are correlated with south-westerly winds, because the moisture easily penetrates into the valley.

(a) Histogram of wind direction and wind speed (total matrix)



(b) Box & Whisker Plot for TSP vs. wind direction (total matrix)

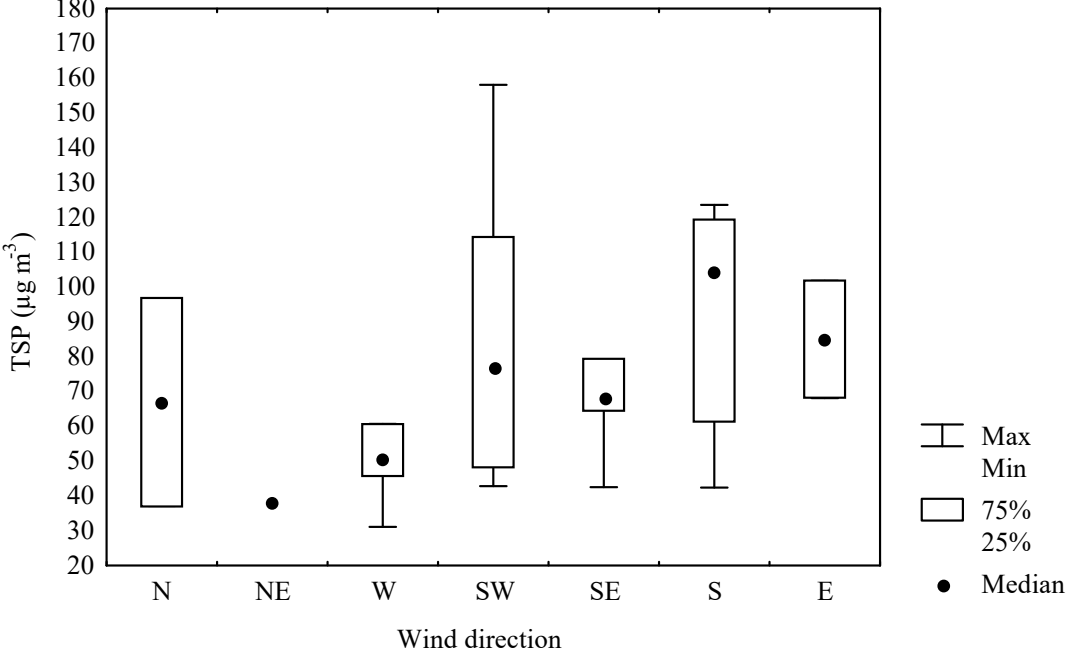


Fig. 1. (a) Frequency of wind direction, values of median, maximum, and minimum for wind speeds for all samples. (b) Distribution of TSP levels according to the wind directions with values of median, maximum, minimum, and quartiles.

3.2 Basic analytical parameters

In order to know the levels of particles and metals, they are also included in the basic statistics of *Table 1*. The mean value of  $78.7 \mu\text{g m}^{-3}$  for TSP is from  $50\text{--}150 \mu\text{g m}^{-3}$ , that would correspond to an “acceptable” air quality according to European directive 1999/30/EC for PM10 particles, but not a “good” air quality (under 50). If the mean value of A particles is subtracted from TSP, the resulting mean value, which would correspond to PM10 particles (sum of B to F stages), is  $66.6 \mu\text{g m}^{-3}$ , still above  $50 \mu\text{g m}^{-3}$ , the final limit value for 24 h. Two samples of TSP exceeding  $150 \mu\text{g m}^{-3}$ , corresponds to a “poor” air quality, although no PM10 value exceeds this value. 23 samples of 41 exceed the limit value for 24 h in PM10 particles, but additionally 16, 12, and 12 samples exceed this value in PM2.5, PM1, and F particles, respectively. The F particles, with  $D_p < 0.6 \mu\text{m}$ , reaches a maximum value of  $104.5 \mu\text{g m}^{-3}$ . This is relevant, because this size has a high probability of depositing in the alveolar region of the lungs. Remember, that 40% of these 41 samples were collected in rainy days. It is known that the sum of particle concentration of various consecutive filters from a cascade impactor contains errors attributed to a possible accumulation of mass from conversion of gas to particles into the filters. This way, mainly particles lower than  $1 \mu\text{m}$  from this conversion are bound to each stage, increasing the mass of each filter but not changing significantly their percentages regarding the sum. Although this fact exists, it is clear that numerous sum values are much higher than the limit for PM10 particles, even in the sum values corresponding to PM2.5, PM1, and F particles. Because of this effect of accumulation of mass in the sum, we cannot include these PM concentrations as analytical variables in the statistical treatment, except for these comparisons.

In relation to the total metal concentrations, the lead value is five times lower ( $0.097 \text{ ng m}^{-3}$ ) than the limit established by the European Community, however, three samples collected near a foundry exceed this limit of  $0.5 \mu\text{g m}^{-3}$ . Therefore, although lower levels of lead are emitted by leaded fuel driven vehicles, high values can be detected locally in the proximity of foundries, for example the maximum value in *Table 1*. These high mean values of particles and low mean values of metals indicate the important influence of the North Western African particles from the Sahara desert.

### *3.2.1 Total particle content, size distribution, and the effect of rain*

In order to study the differences introduced by the rain in particle and metal levels, *Fig. 2* shows the averaged values of concentrations by comparing dry days and rainy days. The great influence of rain is expressed as percentage.



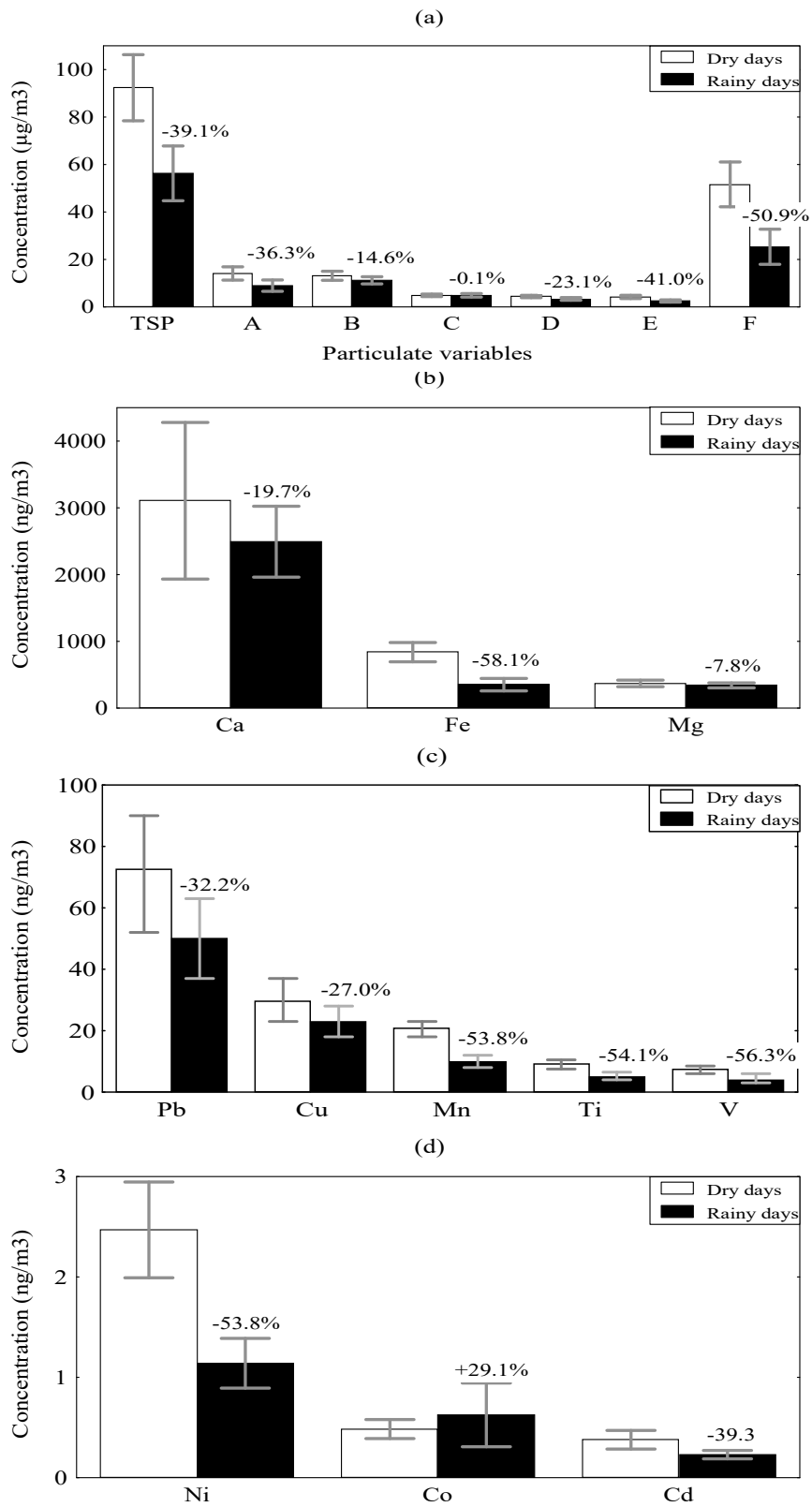


Fig. 2. Averaged values of (a) total suspended particles, TSP, and fractionated suspended particles, FSP, and (b), (c), (d) total metal concentration, TM. Effect or rainfall comparing dry days and rainy days.

Table 2. Correlation coefficients (r) for the three matrices of data formed by the meteorological variables, the total suspended particles (TSP), and their size distribution (FSP, A to F), and the metals (TM)

Meteorological variables				Total and fractionated particle variables								Total metal variables										
WS	AT	AP	PP	TSP	A	B	C	D	E	F	Ca	Fe	Mg	Pb	Cu	Mn	Ti	V	Ni	Co	Cd	
<b>(a) Total matrix</b>																						
WS	1.00	-0.53	-0.48	0.54	-0.39	-0.43	-0.25	-0.07	-0.37	-0.40	-0.35	-0.13	-0.46	0.01	-0.37	-0.38	-0.47	-0.51	-0.41	-0.50	0.10	-0.56
AT	-0.53	1.00	0.38	-0.51	0.62	0.46	0.35	0.22	0.54	0.61	0.64	-0.30	0.61	0.09	0.37	0.47	0.64	0.59	0.35	0.51	-0.32	0.51
AP	-0.48	0.38	1.00	-0.66	0.12	0.02	-0.16	-0.30	0.00	0.10	0.21	0.01	0.27	-0.10	0.11	0.07	0.28	0.30	0.14	0.20	-0.09	0.16
PP	0.54	-0.51	-0.66	1.00	-0.48	-0.46	-0.31	0.07	-0.24	-0.37	-0.48	-0.05	-0.56	-0.06	-0.20	-0.31	-0.57	-0.54	-0.47	-0.50	0.37	-0.28
<b>(b) Dry days matrix</b>																						
WS	1.00	-0.21	0.03	-	0.03	-0.25	-0.07	0.01	-0.02	0.06	0.13	-0.01	-0.01	0.20	-0.27	-0.36	-0.08	-0.07	-0.12	-0.17	0.06	-0.47
AT	-0.21	1.00	-0.28	-	0.47	0.31	0.28	0.40	0.53	0.50	0.46	-0.48	0.35	0.01	0.29	0.44	0.46	0.32	0.06	0.24	-0.65	0.40
AP	0.03	-0.28	1.00	-	-0.67	-0.62	-0.65	-0.53	-0.62	-0.67	-0.56	-0.15	-0.61	-0.39	-0.21	-0.33	-0.69	-0.57	-0.55	-0.57	0.06	-0.27
<b>(c) Rainy days matrix</b>																						
WS	1.00	-0.13	0.63	0.03	-0.36	-0.24	-0.39	-0.33	-0.46	-0.66	-0.29	-0.37	-0.25	-0.07	-0.08	0.04	0.01	-0.39	-0.22	-0.30	-0.10	-0.43
AT	-0.13	1.00	-0.01	-0.42	0.50	0.45	0.37	-0.16	-0.15	-0.13	0.59	-0.45	0.61	0.01	-0.12	0.18	0.20	0.40	0.60	0.31	0.04	0.04
AP	0.63	-0.01	1.00	-0.24	-0.16	-0.15	-0.37	-0.49	-0.50	-0.41	-0.02	-0.29	0.02	-0.17	-0.29	-0.09	0.37	-0.03	0.15	-0.22	0.11	-0.15
PP	0.03	-0.42	-0.24	1.00	-0.35	-0.61	-0.52	0.16	0.21	0.15	-0.28	0.30	-0.44	0.19	0.15	-0.29	-0.41	-0.24	-0.54	-0.38	0.42	0.07

WS: wind speed, AT: ambient temperature, AP: atmospheric pressure, PP: precipitation

Also, single correlations of particles and metals with meteorological parameters are shown in *Table 2*. This table highlights the positive and negative correlation coefficients that indicate the linear behavior between particle and metal concentrations and meteorological parameters. In *Fig. 2-a*, the decrease in concentration of the fine particles (E particles: – 41%, and mainly F particles: – 51%) is greater than that of coarse particles (A particles: 36%, B particles: 15%). However, in *Table 2-c*, the higher anticorrelation with rainfall can be observed for particles larger than 4.9  $\mu\text{m}$ , mainly the A particles  $> 10 \mu\text{m}$  ( $r = -0.61$ ); meanwhile, the value for F particles is low ( $r = -0.28$ ). This fact seems to be a contradiction, but one observes an easy explanation: the fine particles are those that are eliminated in large proportion (–51 % in *Fig. 2-a*) independently of the quantity of rain (– 0.28 in *Table 2-c*). Meanwhile, the coarse particles are those that respond more linearly to the removal and washing effect of the rain (– 0.61 in *Table 2-c*). Thus, fine particles are removed from the atmosphere independently of the amount of rain, whereas elimination of coarse particles is dependent on rainfall values.

On the other hand, in *Table 2-c*, the negative correlation between TSP and rainfall was not as significant as might be expected ( $r = -0.35$ ). This fact can be explained by the differences in the correlation coefficients of the different size fractions (from –0.61 for A particles to +0.21 for D particles). This is one of the aspects that justifies the importance of studying the particle sizes for meteorological and environmental interpretations.

Regarding the influence of rain on metal contents, the lowest values were observed again for the rainy days (*Fig. 2-b,c,d, Table 3*). The percentages for the size fractions of metals can be seen in *Table 3*. In the last file, the highest XXX negative percentages of total concentrations were found for Fe (–58.1%), vanadium (–56.3%), Ni (–53.8%), Ti (–54.1%), and Mn (–53.4%), but on the contrary, high positive percentages of cobalt (+29.1%) were found. The higher values are for fine particles, except for vanadium (–67.0%) and calcium (–51.8%), which are for coarse particles. The high percentages found in rainy samples correspond to the majority of size fractions of cobalt, mainly the E particles, and several fractions of magnesium and cadmium.

We assign these decreases in percentages mainly to two causes: the effect of washing of particles, depending on their size, the solubility of the particles, and the metal compounds contained in them (*Mészáros, 2002*). About their size distribution, we know through our studies on the same samples, that the metals are more associated with the smallest size fraction (F particles) regarding the TSP concentrations, such as Ni (73%), V (70%), and Co (56%), although, other metals also have notable percentages, such as Mg (48%), Mn (44%), Ti (42%), and Fe (37%), always higher than in the percentages of coarse particles (*Fernández et al., 2001*). These percentages would explain the large washing effect on metals in the rainy day situations, including Fe and Ti, mainly on fine particles.

Table 3. Percentages of decreases of the concentrations of particles and metals by the rain regarding the dry days

	TSP	Ca	Fe	Mg	Pb	Cu	Mn	Ti	V	Ni	Co	Cd
A	-36.3	-51.8	-54.5	-9.8	-39.1	-29.8	-49.9	-50.4	-67.0	-44.7	+9.7	-22.9
B	-14.6	-47.3	-43.1	+16.4	-16.6	-17.7	-45.3	-42.0	-45.4	-49.2	-4.2	+14.2
C	+0.1	-3.7	-36.1	+26.3	-25.2	-2.9	-39.2	-39.5	-55.0	-22.2	+37.5	-10.7
D	-23.1	-2.4	-49.9	+5.4	-41.7	-1.7	-51.2	-50.6	-50.7	-39.0	+23.6	-20.9
E	-41.0	-2.2	-62.2	-17.4	-49.8	-11.1	-54.7	-61.1	-48.0	-44.7	+82.4	-38.3
F	-50.9	+6.5	-71.1	-20.2	-30.6	-45.7	-59.9	-62.2	-57.6	-57.4	+33.2	-48.4
<b>Total</b>	<b>-39.1</b>	<b>-19.7</b>	<b>-58.1</b>	<b>-7.8</b>	<b>-32.2</b>	<b>-27.0</b>	<b>-53.8</b>	<b>-54.1</b>	<b>-56.3</b>	<b>-53.8</b>	<b>+29.1</b>	<b>-39.3</b>

With regards to solubility, we know through our chemical speciation studies corresponding to these fine particles samples, that the metals with higher percentages in the soluble chemical forms regarding the total concentrations are those of V (50%), Ni (40%), Co (35%), and Mn (33%), but not those of Fe (4%), Ti (8%), and Mg (18%) (*Fernández et al.*, 2002). These percentages would explain the large decreases in the sample concentrations for the metals V, Ni, and Mn in rainy day situations, specially regarding the high soluble capacity of vanadium. The metals Fe and Ti are not particularly soluble, however, both are removed well enough by rain. Their percentages of decrease in the fine fraction are 71.1% and 62.2%, respectively, higher than V, Ni, and Mn (*Table 3*). Therefore, in the case of Fe and Ti, the removal effect that prevails is the physical washing, since their percentages of the fine fraction from the TSP is greater than the 37%, as mentioned above.

Thus, the removal mechanism most probably combines the physical effect of washing by the drops of rain that fall, together with the solvent effect of the drops of water, which dissolve the soluble compounds that form particles and metals. Additionally, the dissolved and washed metals and particles can also haul other chemical forms and particles with them.

With regard to cobalt metal, it is a highly soluble metal and accumulates in the fine particles, however, with higher concentration in the rainy samples. We found an explanation for this contrary behavior: There is a well-known special characteristic of the complexes of cobalt formed by cobalt (II) chloride and water molecules, they reflect pink colors with water and blue colors without water. If there is increasing rain, the concentration of water molecules that surround the cobalt salts and complexes also increases, and the cobalt mixes with the humid air.

On the other hand, correlations of the rainy days matrix (*Table 2-c*) show only the total concentration of vanadium is clearly dependent on rain quantity ( $r$

= - 0.54), and the higher anticorrelations of its size fractions (*Table 4-c*) correspond to particles larger than 4.9  $\mu\text{m}$ , mainly the V2 fraction ( $r = -0.60$ ) and V6 fraction ( $r = -0.57$ ). Although, other size fractions are anticorrelated, as in the case of magnesium >4.9  $\mu\text{m}$  ( $r = -0.66$  for Mg1 fraction), Fe >10  $\mu\text{m}$  ( $r = -0.60$ ), Mn >4.9  $\mu\text{m}$  ( $r = -0.58$  for Mn1 and Mn2 fraction), and Ti >10  $\mu\text{m}$  ( $r = -0.57$ ), showing that the correlation is always with coarse sizes. Elimination of those sizes is dependent on the value of rainfall, with the exception of vanadium.

Both indicators of decreases in particle-metal levels by rain, percentages (*Fig. 2* and *Table 3*), and correlation coefficients (*Tables 2* and *4*) show that these fractionated particles and metals cited are those that have the same response in the rain. In general, it has been possible to observe that particles and metals of different sizes show different behavior in the rain. Differential responses from other parameters should be verified, as has been done for rain.

### *3.2.2 Influence of the remaining meteorological parameters on particle and metal concentrations and their size distributions*

Firstly, the highest TSP values were observed proceeding from the most frequent wind direction, south and mainly southwest, but not from the strong western winds nor the low eastern winds, as can be seen in the Box & Whisker plot of *Fig. 1b*. Another six Box & Whisker plots, which are not represented here for all particle size fractions show, that F particles follow the same wind direction pattern as TSP with higher levels from the south. This trend is also sharper for A particles but mainly for B particles, both are coarse particles.

The effect, that the wind speed could reduce the TSP concentrations in the air by a removal effect from the airborne particles, is an anticorrelation, but it could also increase their levels if the wind resuspends coarse soil particles, showing positive correlation. This opposite effect should be the cause of the correlation coefficient between the two variables, both being low, although it is negative ( $r = -0.39$ ) in the total matrix and rainy situations ( $r = -0.36$ ), and null in dry situations ( $r = +0.03$ , *Table 2*). However, observing the size fraction data, in the rainy day situations only the fine particles between 1.3 and 0.6  $\mu\text{m}$  present a clear negative coefficient (*Table 2-c*,  $r = -0.66$ ). Therefore, these particles are those that were better dispersed by winds only in rainy situations. In *Table 2-a* the rain have a relationship with high wind speed ( $r = +0.54$ ) and anticyclonic conditions, i.e., lower temperatures ( $r = -0.51$ ) and atmospheric pressures ( $r = -0.66$ ).

Regarding the total metal concentrations, *Table 2* shows in the total matrix that Cd was the most easily eliminated by the wind ( $r = -0.56$ ). Other metals have similar but lower anticorrelations, such as Ti ( $r = -0.51$ ), Ni ( $r = -0.50$ ), Mn ( $r = -0.47$ ), and Fe ( $r = -0.46$ ) in the same matrix, and Cd again ( $r = -0.47$ ) in

dry samples. Cd is the only metal that appears with high anticorrelations in the three matrices.

Table 4. Results of the single linear regression (SLR) for the fractionated metals (FM) in function of the meteorological variables. Table contains the higher values of the coefficient r for each metal

Variable	Equation (Y = a + b X)	Correlation coefficient (r)	t <sub>calc</sub>	Degrees of freedom	t <sub>tab</sub>
<b>(a) Total matrix (41 samples)</b>					
Mn4	Mn4 = - 0.63 + 0.08 AT	+0.69	5.95	39	2.02
Fe5	Fe5 = - 24.89 + 2.57 AT	+0.66	5.49	39	2.02
Ti5	Ti5 = - 0.23 + 0.03 AT	+0.66	5.49	39	2.02
Cd6	Cd6 = 0.39 - 0.02 WS	- 0.50	3.61	39	2.02
Ti5	Ti5 = 0.56 - 0.03 WS	- 0.66	5.49	39	2.02
Ni1	Ni1 = 0.31 - 0.02 WS	- 0.55	4.11	39	2.02
Mn5	Mn5 = 1.47 - 0.07 WS	- 0.54	4.01	39	2.02
Fe5	Fe5 = 50.18 - 2.66 WS	- 0.56	4.22	39	2.02
<b>(b) Dry days matrix (25 samples)</b>					
Co3	Co3 = 0.18 - 0.01 AT	- 0.58	3.41	23	2.07
Mn1	Mn1 = 495.14 - 0.49 AP	- 0.70	4.70	23	2.07
Fe5	Fe5 = 3357.00 - 3.30 AP	- 0.60	3.60	23	2.07
Ti5	Ti5 = 29.57 - 0.03 AP	- 0.56	3.24	23	2.07
Ni6	Ni6 = 172.41 - 0.17 AP	- 0.54	3.08	23	2.07
V5	V5 = 86.93 - 0.09 AP	- 0.58	3.41	23	2.07
Cd5	Cd5 = 0.08 - 0.01 WS	- 0.50	2.77	23	2.07
Ni1	Ni1 = 0.37 - 0.03 WS	- 0.60	3.60	23	2.07
<b>(c) Rainy days matrix (16 samples)</b>					
V2	V2 = 0.56 - 0.01 PP	- 0.60	2.81	14	2.15
V6	V6 = 3.69 - 0.11 PP	- 0.57	2.60	14	2.15
Mg1	Mg1 = 79.01 - 1.44 PP	- 0.66	3.29	14	2.15
Fe1	Fe1 = 120.23 - 3.02 PP	- 0.60	2.81	14	2.15
Mn1	Mn1 = 3.01 - 0.08 PP	- 0.58	2.66	14	2.15
Mn2	Mn2 = 2.57 - 0.05 PP	- 0.58	2.66	14	2.15
Ti1	Ti1 = 1.25 - 0.03 PP	- 0.57	2.60	14	2.15
Fe1	Fe1 = - 361.40 + 24.93 AT	+0.62	2.96	14	2.15
V1	V1 = - 1.55 + 0.10 AT	+0.64	3.12	14	2.15
Cd6	Cd6 = 0.29 - 0.01 WS	- 0.62	2.96	14	2.15
Ti2	Ti2 = 1.84 - 0.08 WS	- 0.57	2.60	14	2.15

About their size fractions, Cd was associated with the fine particles,  $<0.6 \mu\text{m}$ , in the total matrix ( $r = -0.50$ , *Table 4-a*) and in rainy situations ( $r = -0.62$ , *Table 4-c*), and with the fine particles between  $1.3$  and  $0.6 \mu\text{m}$  in dry situations ( $r = -0.50$ , *Table 4-b*). This latter size, the E fraction was also associated with other metals, such as Ti, Mn, and Fe ( $r = -0.66$ ,  $r = -0.54$ , and  $r = -0.56$ , *Table 4-a*). Ni was the only metal found in the coarse particles,  $>10 \mu\text{m}$ , ( $r = -0.55$ , *Table 4-a*;  $r = -0.60$ , *Table 4-b*). Finally, Ti presented high anticorrelations in rainy situations (*Table 4-c*) in the coarse particles, between  $10$  and  $4.9 \mu\text{m}$  ( $r = -0.57$ ). The majority of anticorrelations correspond to fine particles,  $<1.3 \mu\text{m}$ , mainly the E particles, except for the coarse particles,  $>4.9 \mu\text{m}$ , of Ni and Ti. Therefore, the particles most easily removed by the wind, as in the effect of rain, are the PM1 particles, fortunately.

On the other hand, significant positive correlations were found between temperature and TSP levels, i.e., the particle levels being high when temperatures were also high or vice versa. This correlation is well highlighted in the total matrix ( $r = +0.62$ ), but also on the rainy days ( $r = +0.50$ ) and slightly on the dry days ( $r = +0.47$ ) (*Table 2*), therefore, this effect is marked and frequent. The mechanism is logical: when temperature is high, the density and viscosity of air diminish, and this favors the resuspension of particles. In the total matrix, particles smaller than  $2.7 \mu\text{m}$  better correlated with the temperature, mainly the F particles ( $r = +0.64$ ). In the dry samples, the particles  $<2.7 \mu\text{m}$  again better correlated with the temperature ( $r = +0.53$  for D particles), and in the rainy situations only particles  $<0.6 \mu\text{m}$  ( $r = +0.59$ ), correlated the best with the temperature. Therefore, the effect of temperature is more accentuated in the particles of less than  $2.7 \mu\text{m}$ , although this would not be applied to extremely fine particles (e.g.,  $D_p < 0.1 \mu\text{m}$ ), because at this size there is not any resuspension.

The resuspension of particles by high temperatures could be attributed to a drying effect on earth crustal particles of soils and additionally to a decrease in air density and viscosity. Both reasons could facilitate the suspension of particles in the air. Our Regional Government is also aware of these episodes, since the particle concentration often exceeds the level of “not acceptable air quality” in its Air Control and Monitoring Stations. The other coherent explanation could be the Saharan particles coming from the North African warm winds. Also, at high temperatures an important production of fine particles occurs. Therefore, all three suppositions can be valid, and the third is in agreement with the experience of our regional episodes. The first two explanations are in agreement with the present particle size study, because it is most likely that the Saharan particles are coarse when they reach the continent (*Schütz and Sebert, 1987; Molinaroli et al., 1993*). This problem exists not only in our city but also in other cities of our region of Andalusia. The Saharan input represents a problem in other Mediterranean countries, including as far away as

Central Europe. Therefore, the new Directive contemplates the possibility of keeping in focus the different geographical situations (Article 5.4 of the *Council Directive 1999/30/EC*, 1999).

Studying the relationship between temperatures and metal concentrations, one found that earth crustal metals such as Mn, Fe, and Ti had high concentrations at high temperature values ( $r = + 0.64$ ,  $r = + 0.61$ ,  $r = + 0.59$ , respectively, *Table 2-a*). This fact supports the two explanations above mentioned, because both particle sizes are coming from earth crustal sources. When we studied their size distribution (*Table 4-a*), we observed that the effect rebounded on Fe5 particles ( $r = + 0.66$ ), Mn4 particles ( $r = + 0.69$ ), and particles of Ti  $< 2.7 \mu\text{m}$ , mainly Ti5 ( $r = + 0.66$ ), i.e., the fine metal fractions again, contained in PM2.5. However, in rainy samples (*Table 4-c*), the size fractions, that have high correlation, are the particles  $> 10 \mu\text{m}$ , such as Fe1 ( $r = + 0.62$ ) and V1 ( $r = + 0.64$ ), i.e., the coarse particles that respond to high temperatures in rainy situations.

On the other hand, we observed (*Table 2-b*), that, contrarily, cobalt was negatively correlated with temperature ( $r = - 0.65$ ), showing behavior opposite to that of TSP, Mn, Fe, and Ti. The size fraction that followed this trend was represented by particles between  $4.9 - 2.7 \mu\text{m}$  ( $r = - 0.58$ , *Table 4-b*). The explanation could be related to the stability of the cobalt complexes in the rainy situations mentioned above. Since temperature is negatively correlated with rainfall and cobalt is positively correlated with rainfall, logically cobalt is anticorrelated with temperature.

Regarding the atmospheric pressure parameter, the correlation study also reveal a dispersion effect on TSP (*Table 2-b*,  $r = - 0.67$ ). This effect of the anticyclonic conditions was strongest for the fine E particles (*Table 2-b*,  $r = - 0.67$ ), but the anticorrelations are high for all size fractions.

There were also several anticorrelations for metal concentrations (*Table 2-b*), with Mn ( $r = - 0.69$ ), Fe ( $r = - 0.61$ ), Ti ( $r = - 0.57$ ), Ni ( $r = - 0.57$ ), and V ( $r = - 0.55$ ). Studying their size distribution (*Table 4-b*) we found, that predominant size fractions for Mn were particles  $> 4.9 \mu\text{m}$  ( $r = - 0.70$  for Mn1 particles), particles  $< 1.3 \mu\text{m}$  for Fe ( $r = - 0.60$  for Fe5 particles), Ti5 particles ( $r = - 0.56$ ), Ni6 particles ( $r = - 0.54$ ), and V5 and V6 particles ( $r = - 0.58$  for V5 particles).

One can observe that the metals having correlations or anticorrelations with the main meteorological parameters are always the earth crustal elements Fe, Ti, and Mn. In these cases not only fine particles were highly correlated, but also the coarse particles in several metals.

Correlations and anticorrelations of particles metals, and their size fractions were found, which could explain several relationships with meteorological parameters. Atmospheric pressure has shown stronger dispersion effect than wind speeds on suspended particles and metals, and temperature shows a contrary effect on concentration. But, in some analytical variables there are negative and positive correlations at the same time. For example, in the rainy



matrix, vanadium is correlated with ambient temperature and anticorrelated with atmospheric pressure, and the same fact occurs in total and dry matrices with TSP, Fe, Mn, Ti, and Ni concentrations. Therefore, what will the global behavior of these elements be, faced with both parameters at the same time? This question can not be answered by single correlations, but with multiple regressions.

### *3.3 Multiple linear regression analysis to correlate the behavior of variables with meteorological conditions*

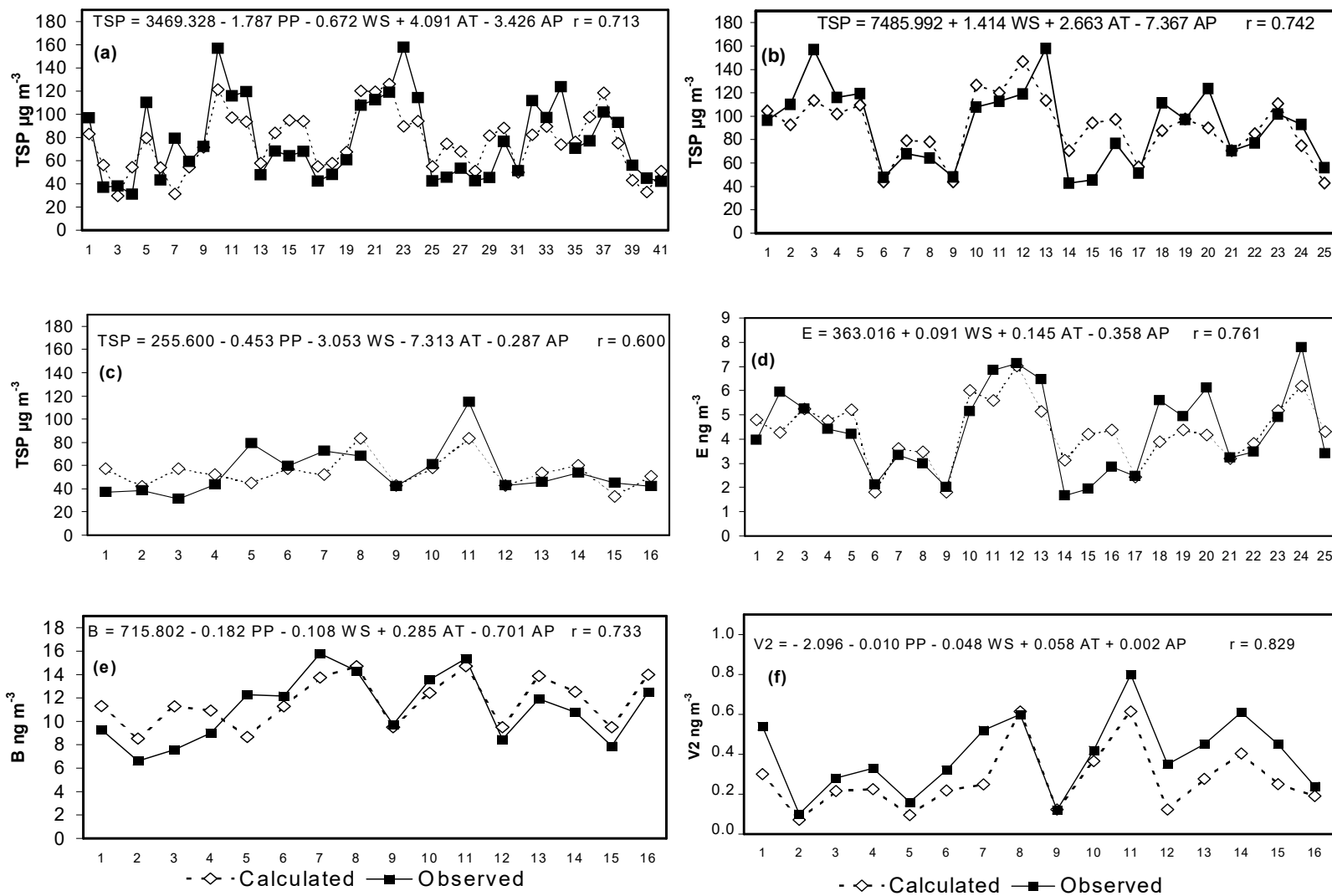
In the previous section, we found significant correlations between analytical variables and meteorological data through simple linear regression (SLR) analyses, mainly with rainfall, temperature, and atmospheric pressure. As expected, it was also possible to find multivariate equations to relate only the correlated variables in the SLR (*Tables 2 and 4*) with all the meteorological parameters at the same time using the multiple linear regression (MLR) analysis (*Fernández et al., 2000*). These equations can be useful in verification if the concentrations in the air can follow a basic model of behavior for particles metals, and their size fractions, and if this model is more accurate than the SLR. Therefore, applying the *Statistica* package we obtained these equations for the three matrices (*Table 5*). This table shows, also underlined, the significant coefficients for meteorological parameters.

One can observe in *Table 5*, that the equations that give the worst correlation coefficients for TSP concentrations are those obtained for the rainy days matrix ( $r = 0.60$ ). Consequently, the coefficient is lower for the total matrix ( $r = 0.71$ ), which contains rainy samples, than for the dry days matrix ( $r = 0.74$ ), without rainy samples. This is also evidence, that rain situations distort the study of atmospheric pollution a lot by total suspended particles. This difference can be verified in *Fig. 3-b,c*, where the poor capacity of prediction of the equation on rainy days can be seen in relation to the dry days. This fact should be due to the different behaviors of the different size fractions in rainy situations most influenced by the rain. Thus, variability (*Table 1*) in rainfall variable (168 %) is greater than wind speed (44%) for example, and, therefore, the success of prediction is lower. Only several fractions of soluble elements such as magnesium or vanadium (*Fig. 3-f*) have a better capacity for prediction in rainy day matrices.

Table 5. Results of the multiple linear regression (MLR) for the TSP, FSP, TM, and FM variables in function of all meteorological variables. The table underlines the significant coefficients for meteorological parameters

Variable (Y)*	a	b <sub>1</sub>	b <sub>2</sub>	b <sub>3</sub>	b <sub>4</sub>	Correlation coefficient (r)	t <sub>calc</sub>	Degrees of freedom	t <sub>tab</sub>
<b>(a) Total matrix (41 samples)</b>									
TSP	3469.328	<u>-1.787</u>	-0.672	<u>4.091</u>	<u>-3.426</u>	0.7128	6.35	36	2.028
F	1334.967	-1.015	0.208	<u>3.036</u>	-1.339	0.6855	5.88	36	2.028
Mn	497.983	<u>-0.427</u>	-0.264	<u>0.914</u>	-0.491	0.7212	6.50	36	2.028
Mn4	1.569	-0.013	-0.020	<u>0.056</u>	-0.001	0.7372	6.81	36	2.028
Fe	22467.817	<u>-19.666</u>	-13.169	<u>35.747</u>	-22.125	0.7001	6.12	36	2.028
Fe5	469.961	-0.509	-1.124	<u>1.720</u>	-0.461	0.7323	6.72	36	2.028
Ti	166.131	-0.154	-0.230	<u>0.311</u>	-0.161	0.6766	5.74	36	2.028
Ti5	3.216	<u>-0.004</u>	-0.018	<u>0.015</u>	-0.003	0.7655	7.43	36	2.028
Cd	8.653	0.001	<u>-0.027</u>	0.016	-0.008	0.6323	5.10	36	2.028
Cd6	4.314	0.000	-0.016	<u>0.014</u>	-0.004	0.5874	4.53	36	2.028
Ni	90.505	<u>-0.055</u>	-0.096	0.069	-0.088	0.6448	5.27	36	2.028
Ni1	8.579	-0.001	<u>-0.022</u>	0.001	-0.008	0.5891	4.55	36	2.028
<b>(b) Dry days matrix (25 samples)</b>									
TSP	7485.992	-	1.414	2.663	<u>-7.367</u>	0.7421	6.91	21	2.080
E	363.016	-	0.091	<u>0.145</u>	<u>-0.358</u>	0.7606	7.32	21	2.080
Co	13.169	-	-0.006	<u>-0.038</u>	-0.012	0.6682	5.61	21	2.080
Co3	-1.808	-	0.000	<u>-0.006</u>	0.002	0.5902	4.57	21	2.080
Mn	1830.889	-	-0.017	<u>0.525</u>	<u>-1.799</u>	0.7448	6.97	21	2.080
Mn1	468.513	-	-0.199	0.046	<u>-0.459</u>	0.7741	7.64	21	2.080
Fe	74643.533	-	6.169	17.149	<u>-73.283</u>	0.6445	5.26	21	2.080
Fe6	34607.535	-	16.263	10.551	<u>-34.147</u>	0.6710	5.65	21	2.080
Ti	681.318	-	-0.020	0.137	<u>-0.667</u>	0.5946	4.62	21	2.080
Ti5	25.812	-	-0.012	0.007	<u>-0.025</u>	0.6597	5.48	21	2.080
Ni	242.965	-	-0.059	0.017	<u>-0.237</u>	0.5917	4.58	21	2.080
Ni1	23.130	-	<u>-0.031</u>	-0.004	<u>-0.022</u>	0.7211	6.50	21	2.080
V	1064.356	-	-0.220	-0.145	<u>-1.039</u>	0.5769	4.41	21	2.080
V1	103.101	-	<u>-0.064</u>	-0.019	<u>-0.100</u>	0.6781	5.76	21	2.080
Cd	16.048	-	<u>-0.032</u>	0.014	-0.016	0.5874	4.53	21	2.080
Cd5	1.352	-	<u>-0.006</u>	0.002	-0.001	0.5707	4.34	21	2.080
<b>(c) Rainy days matrix (16 samples)</b>									
TSP	255.600	-0.453	-3.053	7.313	-0.287	0.5996	4.68	11	2.201
B	715.802	-0.182	-0.108	0.285	-0.701	0.7330	6.73	11	2.201
V	-416.026	-0.074	-0.410	0.943	0.406	0.7308	6.69	11	2.201
V2	-2.096	-0.010	-0.048	0.058	0.002	0.8293	9.27	11	2.201
Mg1	6487.662	<u>-1.840</u>	<u>5.547</u>	-1.105	<u>-6.403</u>	0.8180	8.88	11	2.201
Fe	-	-3.521	-24.701	78.671	15.682	0.6804	5.80	11	2.201
	16502.994								
Fe1	-2304.284	-1.997	-5.962	16.904	2.163	0.7630	7.37	11	2.201
Mn1	-214.868	-0.071	-0.134	-0.006	0.218	0.6949	6.03	11	2.201
Ti1	-56.542	-0.019	-0.107	0.064	0.057	0.7333	6.74	11	2.201
Cd6	-3.824	0.000	-0.017	0.000	0.004	0.6364	5.15	11	2.201

\*: Equation:  $Y = a + b_1 PP + b_2 WS + b_3 AT + b_4 AP$



*Fig. 3.* Comparison between concentrations of the experimental values of analytical parameters and the corresponding predicted values for (a) TSP in total matrix, (b) TSP in dry days matrix, (c) TSP in rainy days matrix, (d) E particles in dry days matrix, (e) B particles in rainy days matrix, and (f) V2 in rainy days matrix.

Regarding the size fractions of particles, in the dry days matrix, the E particles are most highly correlated ( $r=0.76$ ). These particles are those, in which more correlation and anticorrelation were found, therefore, they are the particle sizes most influenced by meteorological parameters. In both, total and dry matrices, the fine particles (E and F fractions) are the most easily predicted (*Fig. 3-d* for the E particles). However, in rainy situations, the coarse particles are the best correlated, the A and B particles instead of fine particles (*Fig. 3-e* for B particles). This fact is in accordance with the fact that the coarse particles are those that respond positively to the amount of rainfall, although the fine particles are those that are best removed by the rain independently of the rainfall. Thus, the rainy situations introduce a major difficulty when predicting the behavior or concentrations of fine particles, which are the most harmful.

Regarding the total metal and their size fraction concentrations, in dry and total matrices the metal with the highest correlation is manganese ( $r=+0.74$  and  $r=+0.72$ , *Table 5*), but on rainy days vanadium ( $r=+0.73$ ) is the metal that was found to be a model of behavior more accurate than the SLR. Meanwhile, manganese does not appear in the rainy days matrix because of its low coefficient ( $r$  is significantly equal to zero). The metal iron is the only one that appears with a coefficient higher than 0.64 in the three matrices, and is also the only one that has a higher correlation coefficient in the rainy days matrix ( $r=+0.68$ ), although with smaller differences, than in the dry days matrix ( $r=+0.64$ ).

The corresponding size fractions of metals have generally higher coefficients than the total concentrations, except for several cases, such as Cd6 and Ni1 in the total matrix, and Co3 or Cd5 in the dry days matrix. Many of these coefficients are high or extremely high, for example, Ti5, Mn4, and Fe5 in the total matrix, Mn1 and Ni1 in the dry days matrix, and Fe1, Ti1, and mainly V2 and Mg1 in rainy days matrix, with coefficients higher than 0.82. These metal fractions are the best explained in both matrices (*Table 5*).

These results confirm again the importance of the relationship of the meteorological parameters with the particles and metals depending on their corresponding sizes.

#### ***4. Conclusions***

Interesting interrelations were found that explain the behavior of particles and metals of different sizes in different meteorological conditions: the effect of temperature on the increase of particle concentrations, the effect of atmospheric pressure and wind speed on the dispersion of particles, and the elimination of particles by the rain.

Multiple linear regression technique was notably useful to confirm the poor capacity of prediction on rainy day conditions for particles and metals. The best prediction was observed for metals that can be in soluble forms in the air, such

as magnesium and vanadium. The particles lower than 1.3 micrometers are the most easily predicted when studying the size distribution of particles. The metal concentrations with the highest correlation coefficients in the MLR were observed for fine particles, such as the Fe, Mn, and Ti metals, or coarse particles, such as the Mn, Ni, Mg, Fe, V, and Ti metals.

We conclude that rainfall is the meteorological parameter that most affects particle elimination and metal pollution by physical and chemical washing away of particles. The other meteorological parameters were also observed influencing the presence of different size particles in the air (wind speed, temperature, and pressure). These effects are different for different size fractions.

It would be interesting to extrapolate from these methods, if used in other regions and countries, to the possible data, checking the differences and similarities with their results. Although, our first objective after this study will be to repeat this research for a longer time period with a larger number of samples and several additional meteorological parameters. The study of the size distribution and meteorological parameters constitutes a way to increase the information about the lifetimes of pollutants in the urban air. The satisfactory results of the multiple linear regression technique should be checked into a context of a wide research with a wide sampling period.

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