Experimental and statistical investigations on atmospheric heavy metals concentrations in an industrial area of Southern Italy(*)

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Summary. — In this paper we present experimental protocol and statistical procedures for evaluating atmospheric concentrations of TSP and heavy metals (Cd, Cr, Cu, Fe, Mn, Ni, Pb and Zn) in the area of Tito Scalo (PZ, Southern Italy), a small industrial site, far from urban areas and surrounded by agricultural and naturalistic sites. In order to characterise the concentrations level and the temporal pattern of each pollutant, we have analysed data collected in two field surveys (April-December 1997, April-December 1998) with univariate and multivariate statistical methods. Furthermore we have investigated the relationships between pollutants concentrations and meteoclimatic parameters (temperature and rainfalls).

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1. – Introduction

In a research program aimed at defining a regional environmental recovery plan for air quality, we have focused our attention on Basilicata. It is a region of Southern Italy, with many naturalistic and agricultural resources, where industrialisation processes are taking place (increase of the extractive activities in Agri Valley, development of new industrial areas after the earthquake of 1980, etc.).

Among atmospheric pollutants, we have chosen to monitor the TSP (Total Suspended Particulate) concentrations and their heavy-metals content. TSP is associated with human health problems, it can influence some atmospheric processes and solar radiation transfer. Moreover, it links other toxic elements, as heavy metals, which can both be inhaled by men and fall on foliage and grass and, in this way, come into the alimentary

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(*) The authors of this paper have agreed to not receive the proofs for correction.

chain [1-3]. Furthermore, in the context of our research, we believe that heavy-metals atmospheric concentration is a useful index for air quality in the investigated area. In fact, the site in which we have performed the measures is placed in an industrial area characterised by the presence of many small and medium industrial activities, by the absence of residential units and by low volume of traffic; furthermore it is surrounded by agricultural lands and naturalistic areas (for example, a WWF oasis). In the literature, we can find many papers in which data measured in urban sites or in industrial zones surrounded by urban areas are shown [4-8]. Other authors discuss data monitored in background sites in order to investigate how TSP and related pollutants suffer a long-range transport or to compare these measures with others carried out in very polluted sites [9,10], but there are no data about industrial emissions in agricultural and naturalistic zones far from the urban area.

In this work we present the experimental and the statistical investigation on heavy-metals concentrations in atmospheric particulate in order to characterise the concentration levels and the temporal patterns of each pollutant (TSP and heavy metals). In the following we show in detail the characteristics of the examined area, the sampling and the analytic protocols and we discuss data collected in two field surveys, April-December 1997 and April-December 1998.

2. – Sampling site

The industrial area of Tito Scalo is about 10 km far from Potenza, a small city (about 75000 inhabitants) of Southern Italy. The investigated zone is located 750 m above sea level and it is surrounded by low hills. The climate is colder than the typical climate of Mediterranean regions, with an annual average temperature of 16 °C. Agriculture, pasture and woodlands are prevalent land uses.

The industrial area is characterised by the presence of many small and medium industries. The main activities are building materials production, structural steel manufacture, industrial and agricultural vehicles construction, railway signs production, metallurgical and mechanical industries. There are few commercial activities and there are not residential units. Railway runs through this zone; the volume of the commercial traffic is low, but the highway SS Basentana is about 1 km far from the sampling area.

3. – Methods

3˙1. *Instrumentation and sampling protocol*. – Our experimental test site includes a TSP sampler and a station for measuring meteoclimatic parameters. Meteorological parameters, temperature and rainfall, are recorded every 5 minutes and, actually, we are updating the instrumentation to measure speed and direction of the wind and the relative humidity in the air.

The sampling and the mass measurement of particulate are performed by means of a low-volume β-gauging sampler placed in an insulated box [11]. It is made up of four main sections: a selective inlet positioned 3.5 m above ground level; a sequential unit for 12 filters; a β-gauge system for measuring mass of particulate deposited on the filters; a pumping system. We use ester cellulose filters (Gelman filters) with a porosity of 0.8 μm and a diameter of 47 mm. The sampling starts at 6 p.m. and the total sampling time is 24 h (one filter every day). The air flow rate is 20 l/min and it is constant and standardised (25 °C and 1013 mb). The β-time for the mass measure deposited on the filter is 15 min.

3˙2. *Chemical protocol*. – After the sampling, each filter is analysed for its content of eight heavy metals (Cd, Cr, Cu, Fe, Mn, Ni, Pb and Zn). The elemental analysis is performed by AAS (FAAS for FeMn and Zn; GFAAS for Cd, Cr, Cu, Ni and Pb). This technique requires a chemical treatment of the filters. Each filter is put in a closed PTE bottle with $3\,\mathrm{ml}$ of HNO_3 and a drop of HF. The bottle is put in the temperature bath at $70\,^\circ\mathrm{C}$ for $20\,\mathrm{min}$. After this, the bottle is opened and is put again in the temperature bath at $100\,^\circ\mathrm{C}$ for $1\,\mathrm{hour}$ until red vapours disappear, then the solution is diluted with $25\,\mathrm{ml}$ of deionized water. The blank contribution from filters and reagents has been evaluated and taken into account (for all the measured elements, the blank values are less than 10%).

4. – Results

4˙1. *Explorative statistical analysis*. – The explorative statistical analysis is the first step for studying an environmental data set. The descriptors we have taken into account are daily atmospheric concentration of eight heavy metals (expressed in $\mu\mathrm{g/Nm}^3$) and TSP daily concentration (expressed in $\mathrm{mg/Nm}^3$). For the k-th year ($k = 1, 2$), all the measured data are organised in matrices (sampling days $\times$ descriptors) in which the element $x_{k,j}^i$ represents the concentration of i-th descriptors ($i = 1, \ldots, 9$) in the j-th day ($j = 1, \ldots, 365$). Furthermore we have built up the matrix M_{TOT}, with dimensions [730,9], including all the measured data.

For each descriptor, the statistical parameters of data distributions (mean m_k^i, median md_k^i, standard deviation sd_k^i, skewness S_k^i and range R_k^i) have been calculated for 1997 and 1998 (table I). The temporal patterns of pollutants concentrations are shown in figs. 1a)-i), in which we plot 1997 and 1998 data one by one.

Regarding TSP concentrations, we note that the observed annual average concentrations, $0.08\,\mathrm{mg/Nm}^3$ for 1997 and $0.05\,\mathrm{mg/Nm}^3$ for 1998 (table I), are higher than others measured in background and remote sites [12], but, on the contrary, both in 1997 and in 1998, we note that the highest suspended particulate concentrations are measured in spring and in summer and this behaviour is typical of mountainous and rural areas [13]. So our results agree, contemporaneously, with the presence of many industrial activities and with site location in a rural zone.

Comparing heavy-metals concentrations data with values found in the literature, we note that the concentration values of Cd, Cr and Pb are lower than values measured in anthropised areas and that Cu and Zn concentrations are comparable with those measured in industrial areas. For other elements, Fe, Mn, and Ni, we find concentrations that are included between values measured in background sites and in polluted sites [14-16].

4˙2. *Univariate analysis of daily concentrations*. – Concerning daily values, temporal patterns of TSP and heavy-metals concentrations are shown in figs. 1a)-i). From these plots, we can already point out a different behaviour among pollutants. Cr seems to be the only one that follows a seasonal trend as TSP concentrations; some elements, as Cu, show very high concentration peaks which are not so evident in other metals.

These differences can be quantified by means of the frequency distributions and the rank distributions analysis. We have determined the frequency distributions of each pollutant. Starting from the observed shape, we can divide the descriptors into two groups: the first, including TSP, Cd, Cr, Fe, Ni and Zn, shows a Gaussian-like distribution; the second, including Cu, Mn and Pb, shows a pattern similar to a log-normal distribution. In fig. 2 two examples of frequency distributions with different shapes are represented.
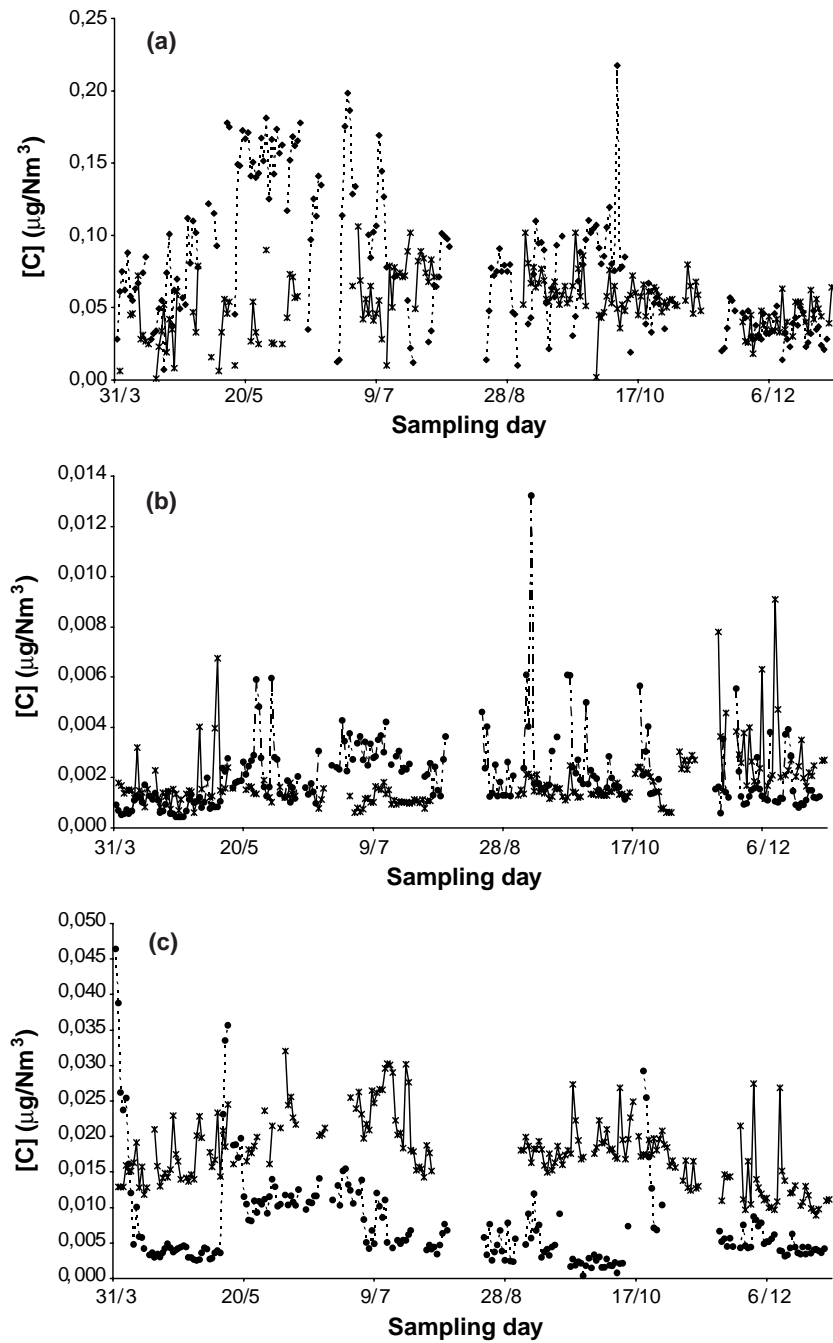
Fig. 1. – Temporal pattern of pollutants' daily concentrations (1997: dashed line, 1998: solid line). a) Total suspended particulate, b) cadmium, c) chromium, d) copper (in the zoom we show values lower than $0.2\,\mu g/Nm^3$), e) iron, f) manganese (in the zoom we show values lower than $0.2\,\mu g/Nm^3$), g) nickel, h) lead, i) zinc.
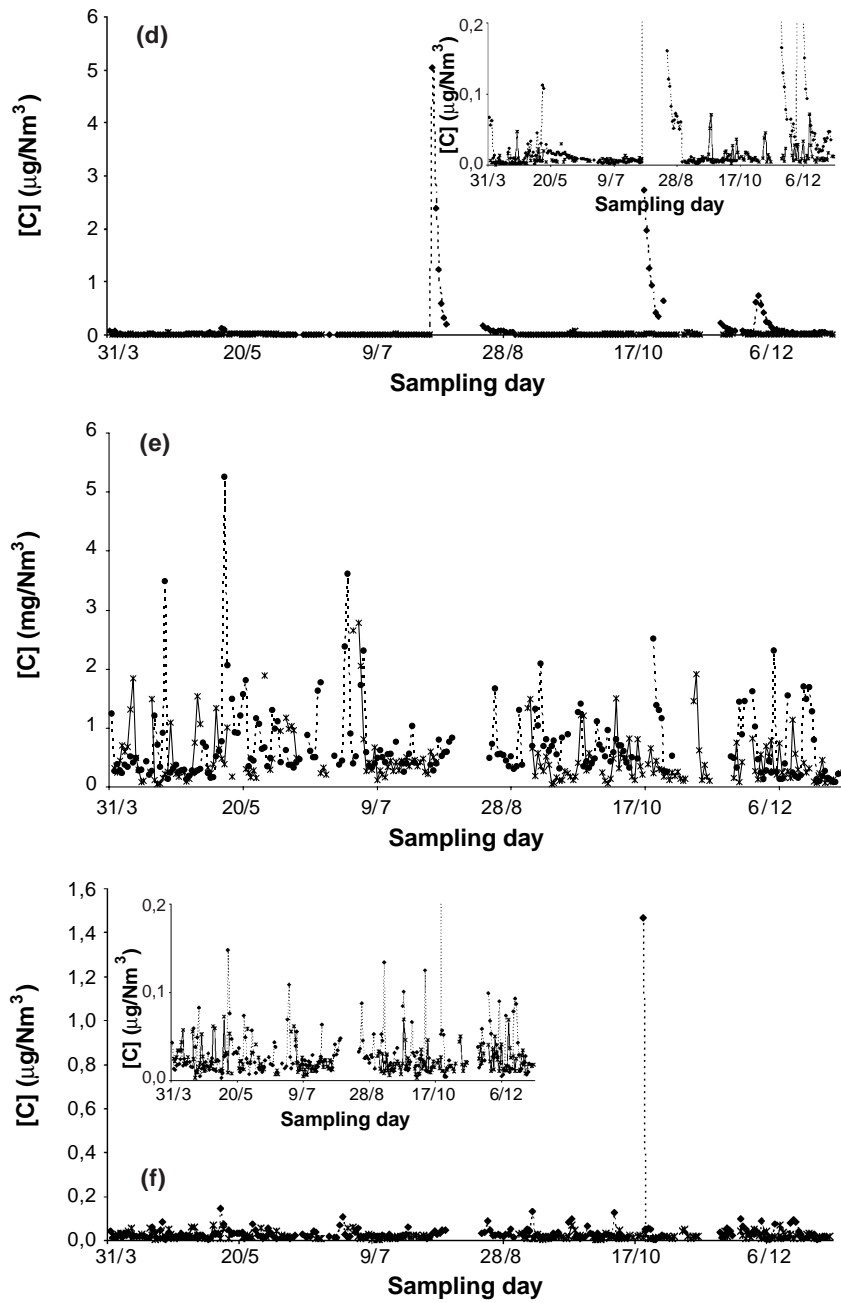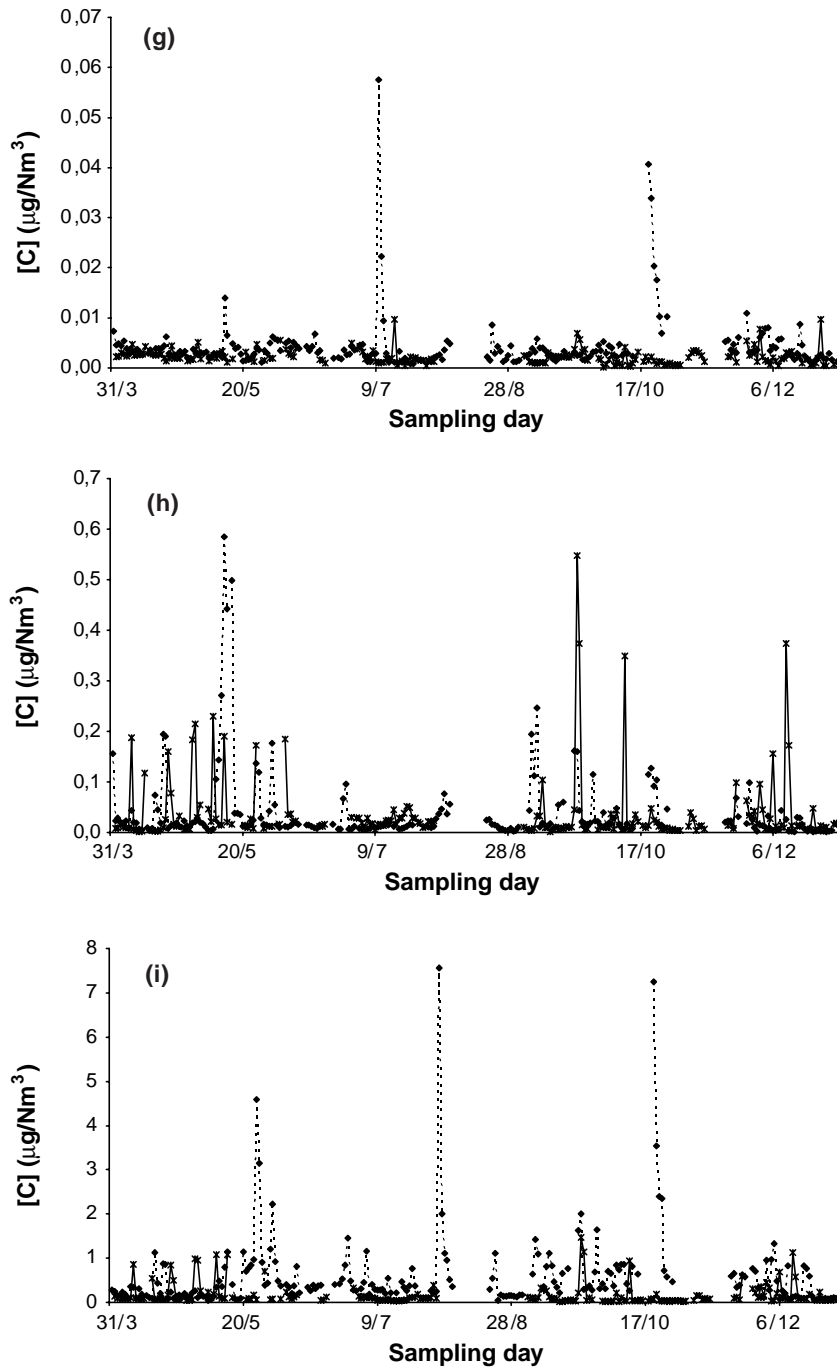
Fig. 1. – *Continued.*

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TABLE I. – *Statistical parameters of daily concentrations distribution. (Legend: Y = year, N = number of measures, m = mean value, md = median, sd = standard deviation, S = skewness, R = range).*

	Y	N	m	md	sd	S	R
Cd	1997	203	0.002	0.002	0.001	3.0	0.0004–0.01
	1998	185	0.002	0.002	0.001	3.3	0.0006–0.009
Cr	1997	203	0.008	0.005	0.007	2.7	0.0004–0.05
	1998	185	0.02	0.02	0.005	0.6	0.009–0.03
Cu	1997	202	0.13	0.01	0.5	7.2	0.002–5
	1998	185	0.01	0.01	0.01	3.3	0.0001–0.07
Fe	1997	203	0.7	0.5	0.6	3.0	0.09–5
	1998	185	0.5	0.3	0.5	2.3	0.04–3
Mn	1997	203	0.04	0.02	0.1	13.1	0.003–2
	1998	185	0.02	0.02	0.01	1.6	0.003–0.07
Ni	1997	203	0.004	0.003	0.006	6.2	0.001–0.06
	1998	185	0.002	0.002	0.001	2.1	0.0001–0.01
Pb	1997	203	0.04	0.02	0.07	4.7	0.002–0.6
	1998	185	0.04	0.02	0.07	4.2	0.002–0.5
Zn	1997	202	0.6	0.4	0.9	5.2	0.05–8
	1998	185	0.2	0.1	0.2	3.0	0.009–2
TSP	1997	188	0.08	0.07	0.05	0.7	0.01–0.2
	1998	185	0.05	0.05	0.02	−0.03	0.001–0.1

In order to characterize this behaviour better, we introduce the rank distributions analysis. For each element, the rank distribution can be easily visualised plotting measured concentrations in decreasing order. The distribution shape of elements with normal-distributed fluctuations around the mean (absence of concentration peaks) is very different in comparison with the distribution shape of elements with asymmetric distribution (presence of concentration peaks). In the first case the rank distribution fits well with an exponential law, in the second one, it fits well with a power law [17]. Applying this test on M_{TOT} matrix, we point out two groups of elements: (Cu, Mn, Pb), which show rank distribution fitted by a power law (for example, the Cu rank distribution is shown in fig. 3a)); (Cd, Cr, Fe, Ni, Zn, TSP), which show rank distribution fitted by an exponential function (for example the Zn rank distribution is shown in fig. 3b)). For all the examined elements, the fit parameter R^2 is higher than 0.85.

Furthermore, in order to investigate the temporal distribution of concentration peaks, we have repeated the rank analysis on 1997 and 1998 data one by one. The results are presented in the upper part of table II: the symbol $\otimes$ indicates the case in which the rank distribution shape does not change from 1997 to 1998. It can be seen that, for Cd, Mn, Ni and Zn, the shape of rank distribution changes, so, for these elements, the occurrence of the concentration peaks has a spot behaviour. For other elements, instead, we observe a similar behaviour in all the examined periods, in particular for Cu and Pb peaks occur both in 1997 and in 1998. These differences are probably due both to

TABLE II. – *Comparison between 1997 and 1998 data sets: for t- and χ^2- tests the symbol* ● *indicates the cases in which the null hypothesis is satisfied; for ranks analysis the symbols* ⊗ *indicates the cases in which the rank distribution does not change.*

	Cd	Cr	Cu	Fe	Mn	Ni	Pb	Zn	TSP
Rank-d		⊗	⊗	⊗			⊗		⊗
t-test							●		
χ^2-test	●		●	●	●	●	●	●	

different mechanisms of emission and to the presence of different emissions sources in the investigated area.

For pointing out other features in temporal pattern of daily concentrations, we have applied a combination of two hypothesis tests (a χ^2-test and a two-tailed pooled t-test with the same significance level ($\alpha = 5\%$) to compare, for each element, data distributions and annual average concentrations obtained from 1997 and 1998 field surveys [18].

For i-th descriptors, in order to compare data distributions, we indicate with d_j the j-th sampling day and we define M^i as the dimension of the intersection set

$$(1) \qquad \{x_j^i\}_{k=1} \bigcap \{x_j^i\}_{k=2}$$

and we calculate

$$(2) \qquad \chi^2_{\exp} = \frac{\Sigma_{j=1}^{M^i}(x_{1j}^i - x_{2j}^i)^2}{(sd_1^i)(sd_2^i)},$$

in which the standard deviations sd_k^i are calculated on M^i elements.
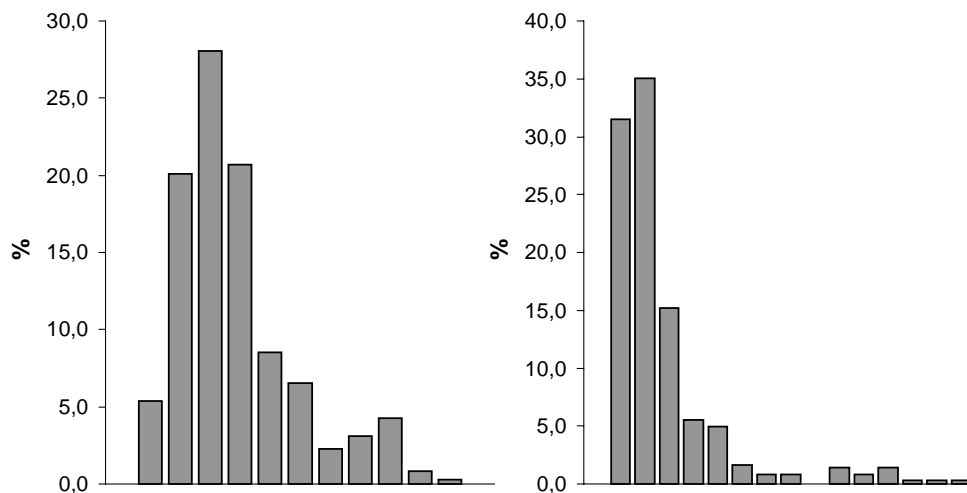

Fig. 2. – Frequency distributions for TSP (left) and lead (right).
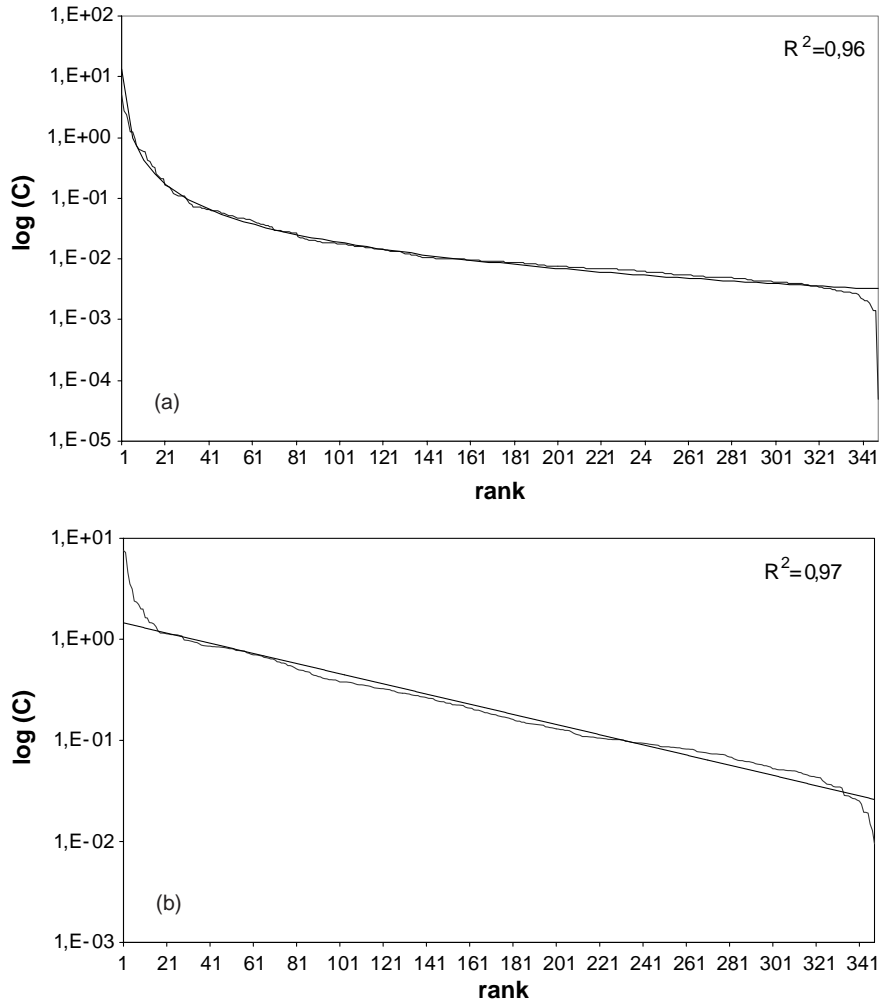
Fig. 3. – Experimental rank distributions and fit: a) copper and b) zinc.

Furthermore, for comparing 1997 and 1998 average concentrations, we calculate

$$(3) \qquad t_{\exp} = \frac{m_1^i - m_2^i}{\sqrt{(sd_1^i)^2/N_1^i + (sd_2^i)^2/N_2^i}} \,,$$

in which N_k^i represents the number of measures of the i-th descriptor in the k-th year. For this t-test the number of degrees of freedom depends on sd_k^i and N_k^i:

$$(4) \qquad \mathrm{df}^i = \frac{\left[(sd_1^i)^2/N_1^i + (sd_2^i)^2/N_2^i\right]^2}{((sd_1^i)^2/N_1^i)^2/(N_1^i - 1) + ((sd_2^i)^2/N_2^i)^2/(N_2^i - 1)} \,.$$

For the i-th descriptor, if $\chi^2_{\exp} < \chi^2_\alpha$ (with $\alpha = 5\%$ and $2(M^i - 1)$ degrees of freedom) we can accept the null hypotheses $\{x_j^i\}_{k=1} = \{x_j^i\}_{k=2}$. In the same way, if $-t_{\alpha/2} \le$

$t_{\exp} \leq +t_{\alpha/2}$ (with $\alpha = 5\%$ and df^i degrees of freedom), we can accept the null hypothesis $m_1^i = m_2^i$ [19].

The results are shown in the lower part of table II: for each test, the symbol $\bullet$ indicates the case in which the null hypothesis is satisfied. We can distinguish different cases: for Cd, Cu, Fe, Mn, Ni and Zn the null hypothesis for the χ^2-test is satisfied while the annual average concentration changes; for chromium and TSP both statistical tests fail; Pb is the only element for which no change is observed between 1997 and 1998. Combining these results with rank distribution analysis, we can note that for elements, as Cd, Mn, Ni and Zn, for which the shape of rank distributions changes, the variations from 1997 to 1998 are due to different occurrence frequencies of peaks. Instead, for the other elements, except for Pb, changes are probably due to a diffuse increase of emissions both from natural sources and from industrial ones. Finally, for Pb, we note a stable behaviour according to the hypothesis that the level of this pollutant is linked to traffic volume that, in the examined periods, does not show significant changes.

4`3. *Bivariate analysis of daily concentrations.* – In order to point out the relationships among all the different descriptors, starting from M_{TOT} we have evaluated Pearson's correlation coefficient ρ^{mn} (with $m = 1, \ldots, 9$ and $n = 1, \ldots, 9$ and $m \neq n$). The correlation matrix is shown in the upper part of table III, in which we have underlined ρ-values ≥ 0.25 (47% of examined cases). This result points out the presence of a complex pattern of relationships among all the descriptors. In particular the highest positive correlation coefficient is $\rho(\mathrm{Cu\text{-}Zn}) = 0.7$, that is probably due to the common industrial origin of these pollutants [20, 21]. We also find positive correlation coefficients between Ni and the couple Cu-Zn and between Ni and Mn, according to the relationships pointed out in the previous analysis.

The positive correlation between Zn and Pb can give us information about traffic emissions. In fact some recent papers suggest to use zinc in addition to lead as marker element for vehicles' emissions [10]. Finally we find a positive correlation between TSP and iron, a typical element of earth crust, so we could assume that, in the investigated area, Fe emissions have mainly natural origin [22].

Furthermore, we can analyse the correlation structure of data by eliminating the influence of concentration peaks. The statistical definition of extreme event (peak) requires either a very high number of observations [23], or the application of multivariate techniques. In a first approximation, it is possible to use an empiric rule: we have chosen to cut on the right the frequency distributions with a confidence level of 1%. In this way, we eliminate the first four values of concentration for each pollutant and we calculate the ρ-coefficients again. The obtained values are shown in the lower part of table III. We can note that, in this case, the correlation between Mn and Cu is not statistically significant and the highest positive correlation coefficient is $\rho(\mathrm{Fe\text{-}Mn}) = 0.8$. These results confirm the hypothesis that some aspects of the correlation structure are related to anthropic emissions while others are due to natural background.

4`4. *Bivariate analysis among pollutants concentrations and meteoclimatic parameters.* – For meteorological variables, from data recorded every 5 minutes, we calculate the average daily ambient temperature T_{A} (°C) and the total daily rainfall Rf (mm). In table IV we show the statistic parameters for 1997 and 1998 data, in particular, for rainfall we use only the values higher than 0.2 mm (35% for 1997 data and 24% for 1998 data).

Concerning the relationships among pollutants and meteoclimatic parameters, in table V we show Pearson's coefficient values. We point out that Cr and TSP concentrations

TABLE III. – *Correlation matrix of particulate and heavy-metals daily concentrations. In the lower part of the matrix the ρ-values calculated without concentration peaks are shown. In parentheses the number of degrees of freedom* (df) *is reported. In bold we indicate the cases in which ρ is statistically significant with a confidence level of* 1% *(we note that* P (df $= 100$, $|r| \geq 0.25) \leq 1$%*).*

	Cd	Cr	Cu	Fe	Mn	Ni	Pb	Zn	TSP
Cd	1	−0.05	0.06	**0.36**	**0.28**	0.17	**0.30**	**0.41**	0.14
		(387)	(387)	(387)	(387)	(387)	(387)	(386)	(350)
Cr	−0.08	1	−0.03	0.16	0.11	0.08	**0.29**	−0.05	−0.03
	(380)		(387)	(387)	(387)	(387)	(387)	(386)	(350)
Cu	0.05	−0.11	1	0.13	**0.40**	**0.35**	0.06	**0.75**	−0.04
	(380)	(380)		(387)	(387)	(387)	(387)	(386)	(350)
Fe	**0.43**	0.10	0.10	1	**0.37**	**0.30**	**0.46**	**0.39**	**0.32**
	(381)	(382)	(380)		(387)	(387)	(387)	(386)	(350)
Mn	**0.55**	−0.04	0.17	**0.79**	1	**0.48**	0.19	**0.58**	0.02
	(381)	(382)	(381)	(383)		(387)	(387)	(386)	(350)
Ni	0.21	−0.08	**0.54**	**0.36**	**0.40**	1	0.19	**0.42**	0.17
	(381)	(381)	(382)	(381)	(382)		(387)	(386)	(350)
Pb	0.31	0.19	0.07	**0.32**	**0.44**	0.22	1	**0.30**	0.13
	(381)	(383)	(380)	(382)	(382)	(381)		(386)	(350)
Zn	**0.49**	−0.19	**0.39**	**0.50**	**0.59**	**0.46**	**0.42**	1	0.18
	(380)	(380)	(382)	(380)	(381)	(382)	(380)		(349)
TSP	0.20	−0.06	−0.07	**0.25**	0.08	0.16	0.04	**0.27**	1
	(343)	(343)	(342)	(344)	(345)	(343)	(343)	(342)	

are positively correlated with ambient temperature. This result confirms the existence of a link between these two elements, already pointed out with univariate and bivariate analysis. In particular we find that, both for 1997 data ($N_1 = 188$) and 1998 data ($N_2 = 162$), the ρ-coefficient is statistically significant, ρ(Cr-TSP)$= 0.3$ and ρ(Cr-TSP)$= 0.3$, respectively.

Finally, we observe that all the correlation coefficient values among pollutants and rainfall are not statistically significant. In particular, in some cases, we find negative

TABLE IV. – *Statistical parameters for meteoclimatic variables (legend:* T_A = *ambient temperature,* Rf = *rainfalls,* Y = *year,* N = *number of measures,* m = *mean value,* sd = *standard deviation,* R = *range).*

	Y	N	m	sd	R
T_A	1997	239	13	7	−1–27
	1998	185	12	6	−1–30
Rf	1997	83	7	12	0.2–65.6
	1998	31	6	11	0.2–66.6

TABLE V. – *Correlation coefficients among pollutants and meteoclimatic parameters In parentheses the number of degrees of freedom* (df) *is reported. In bold we indicate the cases in which* ρ *is statistically significant with a confidence level of* 1% *(we note that for* $T_A P$ (df = 100, $|r| \geq 0.25$) $\leq 1\%$ *and for* RfP (df = 80, $|r| \geq 0.25$) $\leq 2.5\%$).

	Cd	Cr	Cu	Fe	Mn	Ni	Pb	Zn	TSP
T_A	0.17	**0.30**	−0.14	0.21	−0.02	−0.07	−0.03	−0.03	**0.36**
	(269)	*(269)*	*(269)*	*(269)*	*(269)*	*(269)*	*(269)*	*(268)*	*(247)*
Rf	−0.04	−0.05	0.05	−0.09	−0.04	0.03	−0.05	−0.02	−0.09
	(85)	*(85)*	*(85)*	*(85)*	*(85)*	*(85)*	*(85)*	*(85)*	*(81)*

values which could be explained by a scavenging effect of the rain [6]. In fact, analysing monthly behaviour of TSP concentrations, we note that values measured in May 1997 are higher than values in May 1998 and that, at same time, the rainfall measured in May 1997 (about 20 mm) is lower than the rainfall measured in May 1998 (about 50 mm for eleven rain episodes). Furthermore, temperature and TSP concentrations are positively correlated, so we can suppose that, in our test site, the increase of TSP concentrations during hot months may be caused by resuspension of soil dust which increases during the dry season.

4˙5. *Principal component analysis of daily concentrations.* – For PCA, all the measured data are organised in a matrix M'_{TOT} (sampling days × descriptors) in which we have eliminated daily records with data missing:

$$
(5) \qquad M'_{\text{TOT}} = \begin{pmatrix} c_1^1 & \cdots & c_1^9 \\ \cdots & c_j^i & \cdots \\ c_{348}^1 & \cdots & c_{348}^1 \end{pmatrix}.
$$

In this matrix c_j^i represents the concentration of the i-th descriptor ($i = 1, \ldots, 9$) measured in the j-th sampling day ($j = 1, \ldots, 348$). Starting from M'_{TOT} we determine the descriptors association matrix A_{TOT} [9, 9], evaluating for each couple of descriptors Pearson's ρ-coefficient. For determining the principal components (PCs), we calculate eigenvalues ($\lambda_1, \ldots, \lambda_9$ with $\lambda_1 > \cdots > \lambda_9$) and eigenvectors ($\mathbf{a}_1, \ldots, \mathbf{a}_9$) of the matrix A_{TOT} [24].

In our case, only the first three eigenvalues are higher than 1 (table VI). So, we can take into account only the first three principal components, reducing the dimension of our data set from 9 to 3 and explaining 64% of the total variance.

In order to investigate the nature of the PCs, we use the loadings l (the weights of each original descriptor in the new variables) and the co-ordinates of the original variables l^* in the new space of the principal components (table VI). Generally descriptors with loading ≥ 0.5 are considered to be significant elements of a principal component and they can give us information about the physical nature of that component [25].

In table VI, we point out that in the first component Mn and Zn are dominant; in the third component Cr is dominant (it is the only element which has loading ≥ 0.5) and, in this case, we could retain also TSP (it has loading 0.35 that is much more than other l-values). For the second component, we note that there are not dominant elements and that only Pb and Cu have $l > 0.3$; moreover the sign of l^*-values allows us to divide the

TABLE VI. – *Results of PCA for the first three components: eigenvalues (λ); percentages of explained variance (P); loads (l), in bold we indicate values higher than 0.5 and in parentheses we indicate values chosen for a secondary association with dominant elements; co-ordinates (l*), in italic we indicate negative values.*

	I PC		II PC		III PC	
	λ	$P(\%)$	λ	$P(\%)$	λ	$P(\%)$
	3.15	35.0	1.47	16.3	1.15	12.7
	l	l^*	l	l^*	l	l^*
Cd	0.30	0.31	0.03	0.14	0.13	0.33
Cr	0.02	0.08	0.23	0.40	**0.54**	*−0.69*
Cu	0.37	0.34	0.36	*−0.50*	0.03	*−0.16*
Fe	0.44	0.37	0.22	0.38	0.01	0.10
Mn	**0.53**	0.41	0.04	*−0.17*	0.04	*−0.18*
Ni	0.41	0.36	0.01	*−0.10*	0.00	*−0.07*
Pb	0.27	0.29	0.33	0.47	0.04	*−0.18*
Zn	**0.75**	0.48	0.10	*−0.26*	0.00	0.07
TSP	0.07	0.15	0.14	0.31	(0.35)	0.55

pollutants into two groups: (Cu, Mn, Ni and Zn) with negative co-ordinates and (Cd, Cr, Fe, Pb and TSP) with positive co-ordinates.

The factors' interpretation can be facilitated by looking at the plots of sampling days in the new reduced space. In fig. 4, we show the plot of sampling days in the reduced space of the first two PCs. We note that some points have co-ordinates ≥ 1 and they are very far from each other. These points can be identified as unusual observations having different characteristics in comparison with all the other sampling days. In fact, if we examine in detail the concentrations pattern of each unusual observation, we find that one metal at least is characterised by the occurrence of a concentration peak.

In order to improve the pattern characterisation and to point out the role of non-dominant descriptors, we repeat the multivariate analysis in progressive steps in which we eliminate, one by one, unusual observations (concentration peaks). Analysing different runs, we note that the percentage of total variance explained increases. In particular, eliminating 6 records with score ≥ 1 (they are represented in fig. 4 with a different symbol), we find that the percentage of total variance explained increases from 64% to 74%, retaining four principal components. In this reduced matrix, the first component is related to concentrations of Cd, Fe, Mn, Pb and Zn, whereas each of the other components corresponds to a single element (II PC = Cr concentrations, III PC = Ni concentrations, IV PC = Cu concentrations).

At the end, we can get information about sources profiles from these results. The first run suggests us the presence of a well-defined group of dominant elements (Cu, Mn, Ni and Zn) that we can identify as industrial sources profile. In the second run, when we reduce the matrix, we can observe that Cd, Pb and Zn form a well-defined group with
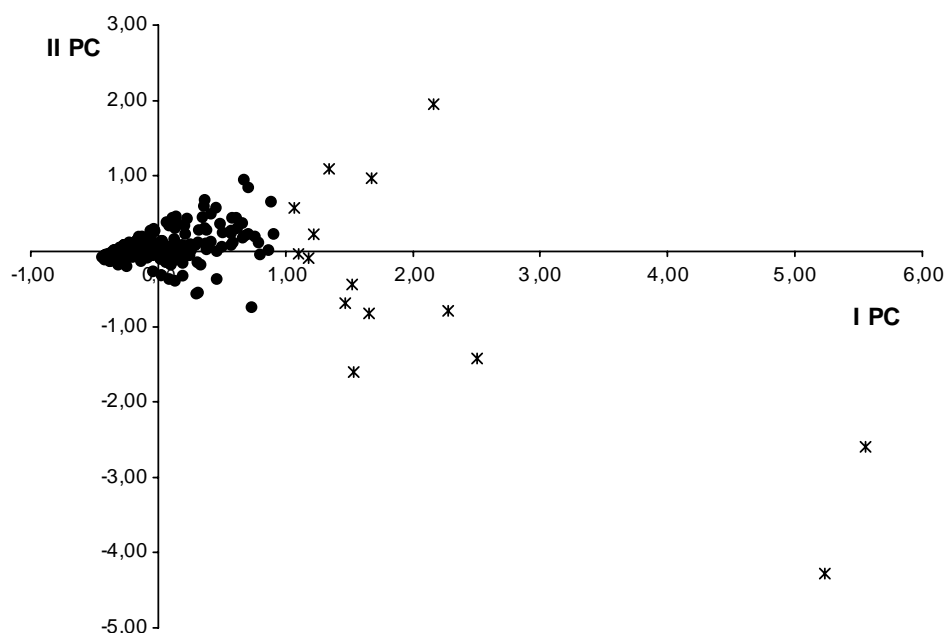
Fig. 4. – Sampling days' plot on I-II principal components.

Fe and Mn. It could be related to a typical background pattern of the investigated areas which includes contributions both from natural sources (particularly linked to Fe and Mn concentrations) and from other anthropic sources, as traffic. Furthermore, as pointed out with previous analysis, Cr and TSP have different behaviours in comparison with all the other pollutants and they do not show a well-defined role in the sources profiles.

5. – Conclusions

In this paper we have presented a preliminary characterisation of atmospheric concentrations of TSP and heavy metals in an industrial area of Basilicata region.

Our experimental procedure (sampling and analytic protocols) is suitable for a correct evaluation of pollutants' level; we are able to measure both low concentrations, for characterising the background level, and concentration peaks. In particular, the statistical analysis, based on frequency and rank distributions, points out that, for some elements, as Cd and Zn, the occurrence of peaks plays a crucial role in the temporal patterns' characterisation.

Concerning the pollutants concentrations measured in our site, we can note that the annual average concentrations of TSP are higher than concentrations measured in areas far from anthropized sites and that the seasonal behaviour is quite similar to the temporal patterns observed in other remote zones, according to both the location of the investigated area and the presence of many small and medium industrial activities.

For heavy metals, we point out different behaviours: for Cu and Zn, we measure concentrations typically observed in industrial areas; for other elements, as Cd, Mn and Ni, we note an increase of annual average concentrations and an episodic occurrence of concentration peaks that may be due to a diffuse increase of industrial emissions

in the area; for Pb, our analysis points out low concentrations which can be mainly ascribed to traffic emissions. For Fe and Cr, a positive correlation with TSP and ambient temperature is underlined; it suggests that further investigation among these elements, natural sources and meteoclimatic variables is necessary to better explain the behaviour of these pollutants.

The multivariate analysis reveals relationships among different elements suggesting us some hypotheses on the pollutants sources. In particular we can identify an industrial sources profile, characterised by Cu, Mn, Ni and Zn, and a natural background profile, characterised by Cd, Fe, Mn, Pb and Zn which becomes dominant when we eliminate the concentration peaks. Actually, for understanding better the relationship among emissions sources, particulate size, concentrations of toxic elements linked to atmospheric particles and meteoclimatic parameters, we are updating the instrumentation adding a particulate monitor with different inlet cut-offs (PM_{10} and $PM_{2.5}$) and sensors for the measure of winds' intensity and direction. Our final goal is to achieve a complete characterisation of the behaviour of these pollutants in order to integrate chemical-physical monitoring procedure with a biological technique based on vegetal species exposed to controlled conditions [26].

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