# Background level of heavy-metals soil concentrations in an industrial area of Basilicata region (Southern Italy)

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**Summary.** — In the framework of Basilicata region air quality monitoring, we are investigating the industrial area of Melfi town. This area has been chosen as test site to evaluate the environmental impact of anthropic activities on a rather unpolluted agricultural area. In this paper we discuss the procedure to characterize the background level of heavy-metals soil concentrations. The topsoil bioavailable fraction of eight elements (Co, Cr, Cu, Fe, Mn, Ni, Pb and Zn) has been collected in two annual surveys (1993 and 1994) on a georeferenced grid, translated in GIS informative layer. Statistical analysis of spatial and temporal patterns is shown in detail.

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## 1. – Introduction

In the last few years a new approach to the evaluation of environmental impact of the anthropic activities has been developed. The monitoring is regarded not only as a tool for data acquisition and landscape control but as the first step to describe the relationships between anthropic activities and environment. Integrated methodologies, which allow to interface databases and models output, have to be developed, in order to compare different biotic and abiotic variables, to update databases, to suggest and to correct resort strategies, by evaluating their effects [1-3].

In the framework of regional environmental planning for Basilicata region (Southern Italy), a protocol for air quality monitoring has been developed [4,5]. Particularly, we are investigating the industrial area of Melfi town as a test site, located in an agricultural zone, in which an automotive plant operates from 1993 and an incinerator will operate before the end of 1997 (SATA-FENICE project). Therefore this area is a good test site for evaluating the environmental impact of a big industrial plant in a rather unpolluted agricultural area with few urban and industrial sites. The

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49

monitoring network provides a combined use of optical, chemical-physical and biological techniques. Furthermore, by means of a Geographic Informative System (GIS), we could manage different databases and interface databases and models. At present, our operative unit is developing a procedure based on bioindicators and chemical-physical monitors for measuring the emissions and the depositions of atmospheric particulate with its heavy-metals content [6, 7].

Here we show the analysis of heavy-metals soil content that, in the absence of previous data about the local level of heavy-metals pollution, is the first step for the background characterization [8-10]. On a large area surrounding the pollution source, in two annual field surveys (autumn 1993 and 1994), we have evaluated the topsoil bioavailable fraction of eight elements (Co, Cr, Cu, Fe, Mn, Ni, Pb and Zn) in a georeferenced sampling grid. The bioavailable fraction is a good indicator for evaluating concentration changes in soil and vegetation due to anthropic stress [11, 12]. In fact heavy metals usually form chemical compounds which are not directly available to the organisms, while the mobile forms (bioavailable forms) tend to increase due to anthropic emissions. Therefore their soil concentrations may vary more rapidly than other descriptors [13, 14]. Furthermore, the evaluation of the heavy-metals bioavailable fraction is particularly important in agricultural zones because its increase may damage plants and crops [12] and modify the cycling of essential micronutrients [15].

A detailed statistical analysis (univariate and multivariate) has been carried out to determine the background soil patterns and to establish a comparison procedure among field surveys, distinguishing between changes due to anthropic activities and natural fluctuations. Furthermore, georeferencing the sampling points and translating the data in informative layers, by means of the GIS, we can obtain a punctual representation of the collected information, that, at this step of the analysis, represents a useful tool in data comparison. A GIS environment will be further on utilized in the future development of this research to optimize experimental and analytical procedures.

## 2. – Materials and methods

2<sup>•</sup>1. Area. – In the industrial area of Melfi town (Basilicata region, Southern Italy) (fig. 1), the FIAT-SATA automotive plant began its production in 1993 (start-up phase) and it is scheduled to produce 1800 veichles per day operating at full capacity. Furthermore, a waste pre-treatment center and an integrated platform for incineration (FENICE project) have been provided to combine waste management and electric-energy production and will operate before the end of 1997 [16].

For background level characterization of heavy-metals soil concentrations, we investigate a large area surrounding the SATA-FENICE site. The examined zone is located at about 350 m above sea level and has an intricate orography; the Ofanto river (W-E direction) runs through it and the north boundaries are fixed by low hills. The area shows an extremely cold climate with respect to the typical climate of Mediterranean zones: the annual average temperature is 13 °C, the rainfalls are most frequent in winter, the prevailing wind directions are North and North-West.

The land use is mainly agricultural. In the North, the zone is planted with cereals and vegetables, in the South-East direction the cultivation of olive trees is prevailing and there are many milk cow farmings. The principal urban sites, Melfi (16 000 inhabitants) and Lavello (13 000 inhabitants), are located in the south zone.



Fig. 1. – Location of the study area.

2'2. Sampling method and analysis. – The samples are collected at 110 sites set radially along eight transects  $(\mathbf{A}, \ldots, \mathbf{H})$ : in the range from 0.5 km to 4 km the sampling distance is 500 m; from 4 km to 8 km the sampling distance is 1000 m. The georeferenced sampling grid is shown in fig. 2.

At each sampling point, at least 5 m from the road edge, an area of  $1 \text{ m} \times 1 \text{ m}$  is selected and the four corn-samples of surface soil (5–10 cm) are collected and mixed to obtain homogeneous samples. Each sample is sealed in polythene bags and frozen.

In soil analysis, acid-extractable metals procedure is recommended for evaluating the bioavailable fraction [17, 18]. The sample soil is dried at 50 °C, then is crushed and passed through a 2 mm sieve. To 10 g dry soil, 100 ml of  $NH_4OAc + distilled H_2O + CH_3OAc + ETDA (pH 4.6)$  solution is added and shaked for 1 h; the extract is filtered and stored in PVC containers, adding deionized  $H_2O$  until 100 ml. This protocol is in accordance with the Italian normative for soil chemical analysis [19].

Two samples for each sampling point are prepared independently. Cu, Fe, Mn, Pb and Zn are analyzed using a Varian AA-1475 flame atomic-absorption spectrophotometer (FAAS), while, for Co, Cr and Ni, a GTA-55 graphite furnace atomic-absorption spectro-photometer (GFAAS) is utilized. Results are based on standard metal solutions using the same acid matrix. Quality control is rigidly observed during the extraction procedure to minimize contamination from air laboratory, reagents or glassware.

In the two solution samples sets, the measured concentrations are statistically compatible, therefore all results are given as averages affected by sensitivity error. In the following the metal concentrations are expressed as  $\mu g/g$  dry weight (ppm DW).

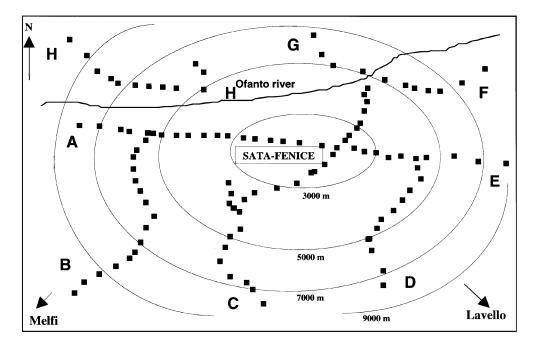


Fig. 2. - Sampling grid.

**2**<sup>•</sup>3. *Data analysis.* – For analyzing spatial and temporal patterns of descriptors (heavy-metals concentrations) an accurate statistical analysis is necessary to distinguish changes due to anthropic stress from natural fluctuations.

For the *t*-th transect  $(t = \mathbf{A}, \dots, \mathbf{H})$  and for the *j*-th metal (j = Co, Cr, Cu, Fe, Mn, Ni, Pb, Zn), the statistical parameters, mean (m), median (md) and standard deviation (s) are calculated. Furthermore, the linear correlation coefficient (r) between heavy-metals concentration and distance from SATA-FENICE site is calculated.

To compare field surveys, for each transect, a two-tailed paired *t*-test and a two-tailed chi-square test, with the same significance level  $\alpha$ , are carried out [20]. Let us indicate with  $(x_1^j, \ldots, x_{n_t}^j)$  and  $(y_1^j, \ldots, y_{n_t}^j)$  the 1993 and 1994 measures of the *j*-th element in the *t*-th transect ( $\sum_t n_t = 110$ ). The statistics  $t_{\exp}$  and  $\chi^2_{\exp}$  defined as

$$t_{\exp} = rac{\sum\limits_{i=1}^{n_t} (x_i^j - y_i^j)}{\sqrt{n_t s_d^2}} , \qquad \chi_{\exp}^2 = rac{\sum\limits_{i=1}^{n_t} (x_i^j - y_i^j)^2}{s_x^2 + s_y^2}$$

(in which  $s_x^2$  and  $s_y^2$  are the data variances,  $s_d^2$  is the variance of differences,  $n_t$  is the samples number in the *t*-th transect) are distributed, respectively, as a *t* variable with  $(n_t - 1)$  degrees of freedom and a chi-square variable with  $2(n_t - 1)$  degrees of freedom. The first compares the average concentrations (null hypothesis:  $m_{tx}^j = m_{ty}^j$ , with  $\alpha = 0.05$ ), the second compares the data distributions (null hypothesis:  $\{x_i^j\}_t = \{y_i^j\}_t$ , with  $\alpha = 0.05$ ).

Spatial patterns are identified by applying two multivariate techniques: clustering and principal-component analysis (PCA) [21]. These methods are mostly used to identify the combined effects of several measured variables and the influence of external variables [22-24]. Many other mathematical methods are available for analyzing spatial data, particularly geostatistical analysis is often used [25-27]. In the geostatistical approach, the soil metal content, like many other geochemical parameters, is regarded as a regionalized variable and the goal of analysis is to interpolate values between sampling points and to evaluate a set of predicted estimates for mapping purpose [28]. This is beyond our purpose, we want to evaluate the background level of the heavy-metals bioavailable fraction in a large area surrounding the industrial site and establish a comparison procedure among different field surveys.

Starting from the data, organized for each annual survey in a  $[110 \times 8]$  matrix, we calculate the resemblance matrix, which has dimensions  $[110 \times 110]$ , by using the Euclidean distance, and the correlation matrix, which has dimension  $[8 \times 8]$ . The clusters (grouping of samples at different hierarchical levels) are determined with the complete linkage algorithm, applied on the resemblance matrix. To point out the dominant elements of each cluster, the centroids  $C_j$  (average concentrations of the *j*-th element calculated on cluster) are compared, by means of the Mann-Whitney test, with the average concentrations  $M_j$  calculated on all samples: if the null hypothesis  $C_j = M_j$  (with  $\alpha = 0.05$ ) is rejected, the *j*-th element may be called cluster dominant [20].

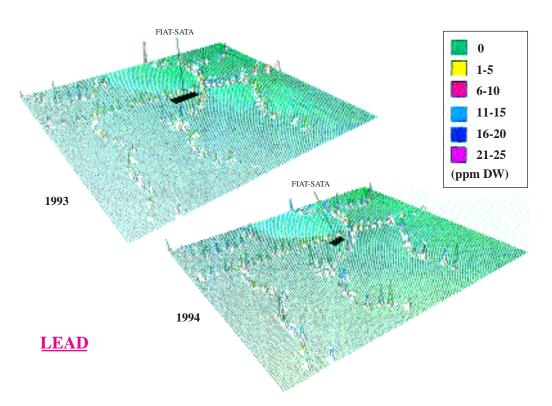


Fig. 3. - Georeferenced maps of Pb soil concentration.

Furthermore, to point out gradients or external forcing, the clusters have been ordered in the reduced space of the principal axes (Principal Component Analysis). The principal components are the eigenvectors of the correlation matrix, the normalized eigenvalues of which,  $\lambda_k^*$  (k = 1, ..., 8), give the explained variance percentages along each component. Bartlett's eigenvalues test is used to distinguish between eigenvalues from field-collected and random data sets [29].

Transect	A	В	С	D	Е	F	G	Н
$n_t$	16	17	22	12	12	14	8	7
Mn 93 Mn 94	$320 \pm 80$ 320 $420 \pm 170$	170	$200 \pm 100$ 180 160 $\pm 90$	$170 \pm 110$ 130 $210 \pm 90$	$250 \pm 80$ 280 $240 \pm 90$	$180 \pm 90$ 130 $180 \pm 70$	$130 \pm 80$ 130 $130 \pm 70$	$160 \pm 30$ 170 130 $\pm 30$
	350	500	110	250	230	180	130	120
Fe 93	$\begin{array}{c} 30 \pm 10 \\ 30 \end{array}$	$\begin{array}{c} 70 \pm 40 \\ 60 \end{array}$	$\begin{array}{c} 100\pm60\\ 100 \end{array}$	$\begin{array}{c} 70\pm30\\ 80 \end{array}$	$\begin{array}{c} 56\pm9\\ 60 \end{array}$	$\begin{array}{c} 130\pm90\\ 90 \end{array}$	$\begin{array}{c} 110\pm70\\ 110\end{array}$	$\begin{array}{c} 80 \pm 20 \\ 70 \end{array}$
Fe 94	$\begin{array}{c} 60 \pm 30 \\ 70 \end{array}$	$70 \pm 20$ 70	$80 \pm 30$ 70	$70 \pm 10$ $70$	$\begin{array}{c} 60 \pm 20 \\ 50 \end{array}$	$\begin{array}{c} 130\pm70\\ 160\end{array}$	$120 \pm 70$ 120	$80 \pm 30$ $60$
Cu 93	$6\pm 2$ 5	$2\pm 1$	$3\pm 2$ 3	$2\pm 2$ 3	$4.9 \pm 0.4$	$3\pm 3$ 2	$2\pm 2$ 2	${3.0{\pm}0.5}\over{3}$
Cu 94	$7\pm 3$ 6	$5\pm 2$ 6	$6\pm 2$ 6	$5 \pm 2 \\ 5$	$10\pm10$ 7	$4\pm1$ 4	$\frac{1}{4\pm 2}$	$5 \pm 1$ 4
Pb 93	$8\pm 2$ 8	$9\pm 1$ 9	$9\pm 3$ 8	$9\pm 1$ 9	$\begin{array}{c} 13\pm 6\\ 12\end{array}$	$11 \pm 3$ 11	$13 \pm 5 \\ 11$	$14 \pm 3 \\ 13$
Pb 94	$9\pm 2$ 9	$\begin{array}{c} 12\pm2\\ 12\end{array}$	$15\pm2$ 15	$\begin{array}{c} 13\pm3\\ 12\end{array}$	$\begin{array}{c} 10 \pm 2 \\ 10 \end{array}$	$\begin{array}{c} 12\pm2\\ 12 \end{array}$	$\begin{array}{c} 13\pm2\\ 14 \end{array}$	$\begin{array}{c} 14\pm1\\ 14\end{array}$
Zn 93	$3\pm 3$ 2	$1.0 \pm 0.3$	$2\pm 1$ 2	$1.7 \pm 0.7$	$6\pm4 4$	$1\pm 1$ 1	$4\pm5$	$2.0\pm0.4$
Zn 94	$\begin{array}{c} 2.6\pm0.9\\ 2\end{array}$	$1.6 \pm 0.2$ 2	$4\pm 3$ 2	$1.9 \pm 0.4$ 2	$3\pm 1$ 2	$3\pm 1$ 2	$7\pm7$ 3	$3\pm 2$ 2
Co 93	$3\pm 1$	$3\pm 2$ 2	$4\pm 2$	$2.8 \pm 0.6$ 2.9	$6\pm 2$	$5\pm2$	$6\pm 2$	$5.5 \pm 0.6$ 5.3
Co 94	$2\pm 1$ 2	$3.6 \pm 0.6$ 3.5	$2\pm 1$ 2	$2.1 \pm 0.9$ 2.2	$1.9 \pm 0.8$ 2.1	$3\pm 1$ 4	$3\pm 2 \\ 2$	$5.5 \pm 1$ 5
Ni 93	$3\pm 1$ 2	$2.8 \pm 0.9$ 2.9	$3\pm 1$	$2\pm 2$ 2	$3\pm 1$ 3	$3.7 \pm 0.6$ 3.8	$3.6 \pm 0.7$ 3.7	$3.3 \pm 0.4$ 3.4
Ni 94	$2.9 \pm 0.9$ 2.7	$7\pm4$ 5	$6 \pm 4$ 5	$\frac{2}{4\pm 2}$	$5 \pm 3$ 4	$8\pm4$	$9\pm 2$ 8	$10 \pm 4$ 11
Cr 93	$0.08 \pm 0.02$ 0.07	$0.07 \pm 0.03$ 0.08	$0.06 \pm 0.02$ 0.06	$0.10 \pm 0.04$ 0.10	$0.04 \pm 0.01$ 0.04	$0.08 \pm 0.04$ 0.07	$0.06 \pm 0.02$ 0.05	$0.07 \pm 0.01$ 0.07
Cr 94		$0.08 \\ 0.14 \pm 0.04 \\ 0.14$				0.07 $0.21 \pm 0.08$ 0.19		

TABLE I. – Statistical parameters,  $m \pm s$  and md, for 1993 and 1994 field surveys.

## 3. – Results

The sampling points are georeferenced using Arc-Info software [30] in order to use a Geographic Informative System (GIS) for data management. The data are translated into GIS data layers; this allows, at the first step of the analysis, to represent heavymetals spatial patterns without utilizing any interpolation function, as shown, for example, in fig. 3, where lead maps, for 1993 and 1994 field surveys, are represented.

For all measured elements, the statistical parameters are summarized in table I. The values of the linear correlation coefficient are shown in table II. Once a significance level (0.01) is fixed, for each  $n_t$  (number of sampling points in the *t*-th transect), there is a value  $r^*$  such that if  $r > r^*$ , the  $n_t$  measures are significantly correlated [31]. In table II, we note that in most of the cases (95% in 1993, 84% in 1994) r is lower than  $r^*$ , *i.e.* in the examined period there is not a significant linear correlation between heavy-metals bioavailable concentration and distance from the industrial site.

Table III shows the results of the statistical tests applied to 1993 and 1994 data sets. By means of the symbols  $\bullet$  and  $\blacksquare$ , we point out the cases in which the null hypotheses are not satisfied. The *t*-test (symbol  $\bullet$ ) points out that in 48% of the examined cases the average concentrations are different,  $m_{tx}^{j} \neq m_{ty}^{j}$  ( $t_{exp} < -t_{0.025}$  or  $t_{exp} > t_{0.025}$ ).

TABLE II. – Values of the linear correlation coefficient; in bold we indicate the cases in which  $P(n_t, |r| \ge |r^*|) \le 1\%$ .

Transect	Α	В	С	D	Ε	F	G	Н
$\overline{n_t}$	16	17	22	12	12	14	8	9
$r^*$	0.7	0.7	0.6	0.8	0.8	0.7	0.9	0.9
1993								
Fe	-0.14	0.55	0.75	0.78	0.23	0.34	-0.25	-0.68
Mn	0.21	-0.50	0.19	-0.29	-0.70	-0.09	-0.12	-0.24
Cu	0.41	-0.22	0.47	-0.57	-0.23	-0.52	0.54	-0.38
Zn	0.37	-0.36	-0.22	0.54	0.90	-0.41	0.60	-0.73
Pb	-0.15	0.62	-0.51	0.26	0.84	-0.14	0.59	-0.33
$\mathbf{Cr}$	0.09	-0.17	-0.07	0.71	-0.46	0.20	0.57	-0.14
Ni	0.23	0.49	0.38	-0.29	0.31	0.14	-0.78	0.28
Co	-0.12	0.63	0.00	0.34	-0.06	0.32	0.21	-0.02
1994								
Fe	0.73	0.24	0.29	0.23	-0.08	0.80	-0.42	-0.69
Mn	0.35	-0.82	-0.51	-0.78	0.31	-0.03	-0.07	-0.68
Cu	0.31	-0.75	-0.34	-0.65	-0.17	-0.76	0.29	-0.57
Zn	0.31	0.35	-0.52	0.66	-0.47	0.04	0.08	-0.43
Pb	0.37	0.40	-0.38	0.66	-0.11	0.64	0.30	0.05
$\mathbf{Cr}$	-0.06	0.49	-0.16	0.84	0.14	0.93	-0.37	-0.48
Ni	0.27	0.83	-0.13	0.73	0.41	0.75	0.53	-0.29
Co	0.31	0.45	-0.55	-0.79	0.58	0.70	0.54	-0.68

	Α	В	С	D	Ε	$\mathbf{F}$	G	Н
Mn	•							
Fe	• •							
Cu	•	• •	• •	•			•	•
Pb	•	• •	• •	• •				
Zn		• •				• •		
Co			•	•	• •	•	•	
Ni		• •	•			• •	• •	• •
Cr		• •	• •	•	•	• •	• •	• •

TABLE III. – Results of statistical tests: the symbol  $\bullet$  indicates the cases in which the null hypothesis of the t-test is not satisfied, the symbol  $\bullet$  indicates the cases in which the null hypothesis of the chi-square test is not satisfied.

Particularly, applying a one-tailed *t*-test (with  $\alpha = 0.05$ ), we can note that  $m_{tx}^j < m_{ty}^j$  in 45% of the cases. The results of chi-square test are shown in table III (symbol **D**), the null hypothesis is not satisfied when  $\chi^2_{exp} < \chi^2_{0.975}$  or  $\chi^2_{exp} > \chi^2_{0.025}$ . We note that in all cases in which the *t*-test hypothesis is satisfied, also the chi-square test does not fail; on the contrary, the chi-square test fails only in 60% of the cases in which the *t*-test hypothesis is not satisfied. In fact the chi-square test, which compares each measure

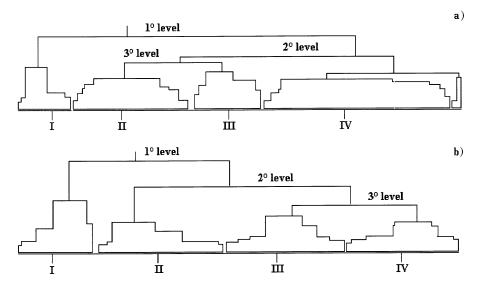


Fig. 4. – Dendrogram of data matrix with dimension  $[110 \times 8]$ : a) 1993; b) 1994.

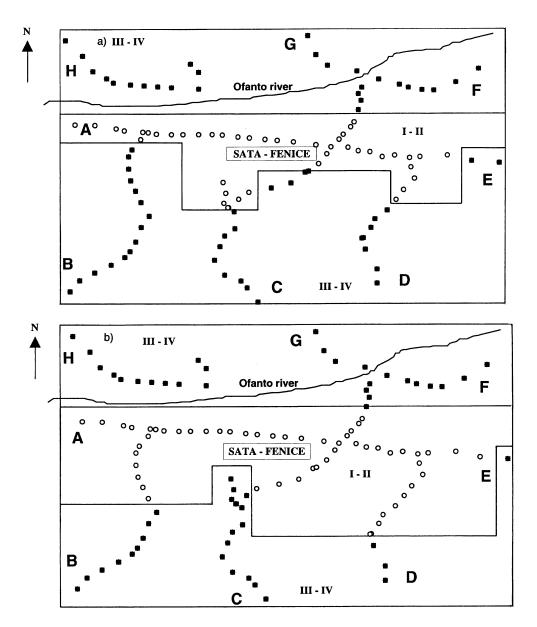


Fig. 5. – Mapping of clusters shown in fig. 4; the symbol  $\blacksquare$  indicates sampling points included in I and II clusters, the symbol  $\bigcirc$  indicates sampling points included in III and IV clusters: a) 1993; b) 1994.

with its corresponding measure in the successive survey, is able to distinguish between the transects in which the changes are equally distributed and the transect in which the changes are localized in one or two sampling points. In these cases, we cannot exclude *a priori* the effect of localized emissions of pollutants which cannot be observed during the sampling procedure.

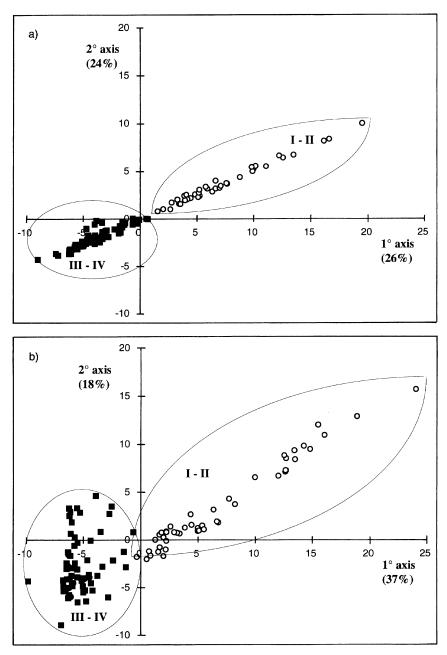


Fig. 6. – PCA plots with 8 descriptors: a) 1993; b) 1994.

In conclusion, only in nineteen cases we point out a significant difference between 1993 and 1994 field surveys. Particularly, we note that Pb and Cu concentrations changes are significant in **B** and **C** transects (south zone) which are near to the principal roads. Ni and Cr concentrations increase in the north zone (area of the Ofanto river, corresponding to **F**, **G** and **H** transects) and in the south zone (**B** transect).

Relative to 1993, the clustering technique points out four groups (the dendrogram is shown in fig. 4a) in which the dominant elements are Mn, Fe and Cu. Relative to 1994, clustering points out a similar pattern (the dendrogram is shown in fig. 4b). At the first and at the second hierarchical level, the groups are still characterized by Mn, Cu and Fe. At lower levels, the grouping depends also on Ni and Cr values, which are dominant in III and IV clusters of 1994 survey. On the grid, for 1993 and 1994, two large subareas may be identified (fig. 5a) and b)): the first, made by III and IV clusters, covers the south and the north zone and is characterized by high Mn and Cu concentrations and low Fe concentrations; the second (I and II clusters) includes A transect and a part of E transect and is characterized by the highest Fe concentrations. PCA patterns comparison (fig. 6a) and b)) shows that, in both cases, the first two principal axes explain about 50% of variance and the clusters have almost the same location relative to these two axes, but in the second survey the points become more spread than in the first survey. Particularly, I and II clusters are located in the first quadrant, III and IV clusters are located in the third quadrant and there is an evident net separation between the samples enclosed in the I and II cluster (sampling points of the central zone) and the others. The spread of points in the 1994 PCA plot may be caused by variations in the concentrations of Pb, Cr, Zn, Co and Ni hidden by Mn, Fe and Cu behavior.

In a successive step, we repeat the multivariate analysis eliminating the dominant elements of the previous classification: Mn, Fe and Cu. Starting from  $[110 \times 5]$  matrices, we determine a new hierarchical grouping (fig. 7). At the first level, the isolated samples, characterized by high concentrations of non-dominant descriptors, such as Zn, have been pointed out. The remaining samples single out two groups characterized by Pb and Co concentrations relative to 1993 and by Pb, Ni and Cr concentrations for the 1994 survey. The 1993 clusters mapping (fig. 8a)) shows that the samples characterized by high concentrations of the dominant elements are concentrated in the north zone (**F**, **G** and **H** transects) and in the first part of **C** and **E** transects. After a year (fig. 8b)) the samples with high concentrations of dominant

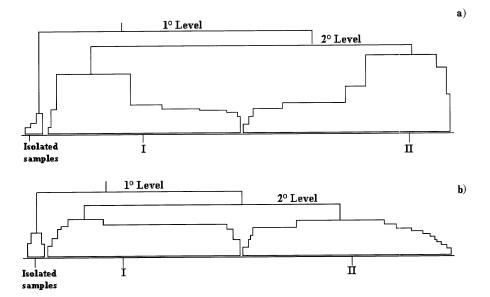


Fig. 7. – Dendrogram of data matrix with dimension  $[110 \times 5]$ : a) 1993; b) 1994.

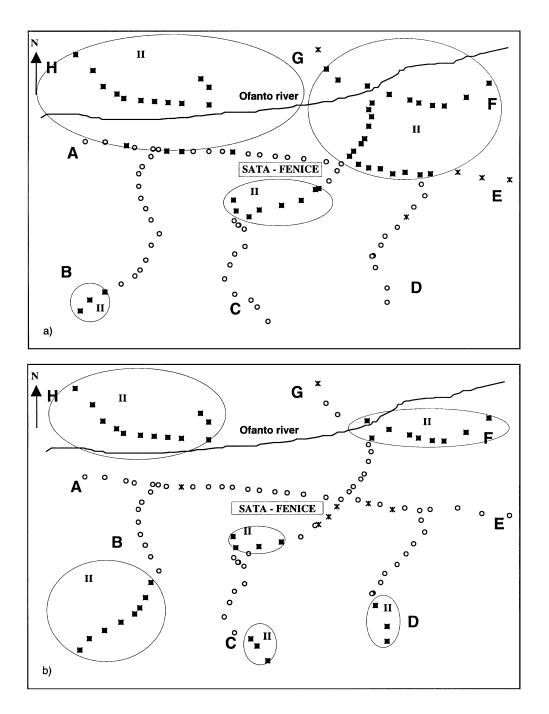


Fig. 8. – Mapping of clusters shown in fig. 7; the symbol  $\odot$  indicates sampling points included in cluster I; the symbol  $\blacksquare$  indicates sampling points included in cluster II, the symbol x indicates isolated samples: a) 1993; b) 1994.

TABLE IV. – Clusters centroids and average distances from the industrial site.

Cluster	Centroid	Distance (km)		
	Pb (ppm DW)	Ni (ppm DW)	Cr (ppm DW)	(1111)
I-94	11	4	0.10	4.3
II-94	14	10	0.20	6.1

descriptors are located in **H** transect and in the external part of **B**, **C**, **D** and **F** transects. Reducing the number of descriptors, the PCA shows a significant separation among groups along the first principal axis (36% is the percentage of explained variance); this confirms that, by separating the samples into two groups, we are able to take into account the significant spatial differentiation.

Finally, to emphasize the role of each element in the spatial patterns evolution, and we carry out again cluster analysis utilizing as descriptors only Pb, Ni and Cr concentrations. For 1993, two clusters have been pointed out based on Pb content: Pb concentrations are higher in **E**, **F** and **H** transects (first cluster) than in the other sampling points (second cluster); instead, Ni and Cr concentrations are distributed more homogeneously. For 1994 at the first level, the samples are divided into two groups relative to the concentrations of all the three chosen elements. Furthermore, we note that, calculating the average distance from the industrial site for each group and comparing these values with clusters centroids (table IV), the sampling points with the highest pollutants concentrations are located far from the line of 5 km. At the second level, the cluster with the smallest heavy-metals concentrations splits up into two subgroups based on different Pb concentrations, as for the pattern of the previous year; instead the second cluster splits up into two subgroups based on different Ni concentrations, reflecting that Ni and Cr changes have a different spatial distribution.

## 4. – Conclusions

In this paper we show the background level characterization of heavy-metals soil concentrations, the procedure to compare different field surveys and the results relative to 1993 and 1994.

The data show that, in the examined zone, the bioavailable fraction of heavy metals in the soil is rather low and that, in the examined period (before of the incinerator start-up phase), there is not a positive correlation between soil concentration and distance from industrial site, along the transects.

The univariate analysis points out that only in few cases significant changes between 1993 and 1994 may be observed. The role of the various descriptors and the influence of external variables can be highlighted by means of multielemental analysis. In fact, taking into account all descriptors, both 1993 and 1994 patterns show a similar trend in which Mn, Fe and Cu are the dominant elements, as accounted for by geomorphologic features of the examined area. In fact these metals are the most diffuse elements and their average concentrations remain almost unchanged. On the contrary, only the 1994 pattern emphasizes the role of minor elements (such as Cr or Ni), which are undergoing stronger variations. By eliminating Mn, Fe and Cu, the effect of endogenous elements is reduced and the spatial evolution of the remaining elements is pointed out.

Local changes in concentrations give useful hints for the evaluation of the environmental impact of the anthropic activities in each subarea. The increase of Pb and Ni concentrations in the south zone stems from an increase in vehicular traffic. In fact in the latest years, the road on the border of the industrial area in the E-W direction (corresponding to A and E transects) has been substituted by a highway, located in the zone of B and C transects. The north zone, which remains spatially homogeneous, also shows an increase of pollutants concentrations, probably linked to orographic and meteoclimatic characteristics of area. In fact, this zone is limited to the south by the Ofanto river and to the north by low hills which form a natural obstacle to the pollutants diffusion. Furthermore, clustering shows the sampling points included in the middle part of C transect, in which high heavy-metals concentrations have been measured. It is the nearest area to the industrial site in the downwind direction.

The results also give us some suggestions for optimizing analysis procedures and samples collection. Regarding the set of descriptors, it may be useful to eliminate the background soil elements, which give few information (as Mn and Fe) and to take into account elements which are more directly linked to the increase of anthropic activities (as, for example, vanadium and cadmium). Furthermore, chemical analysis of specific elements (such as Pb or Cr) may be modified in order to evaluate also soil concentrations of their different forms. Regarding the sampling grid, it may be useful to increase the sampling points in the north zone which is still now strongly cultivated and in the C transect zone, which seems mostly affected by deposition phenomena. In particular, in this area it may be useful to compare heavy-metals content in bioindicators (as roots, leaves, bark) with the soil concentrations.

In conclusion, we would like to emphasize the advantages of utilizing a GIS. By means of thematic layers, it is possible to compare annual field surveys and to overlay the heavy-metals maps with other databases, as digital terrain model (DTM), meteoclimatic and land use maps in order to have a more complete description of the investigated area. Furthermore, it is possible to interface data with models in a GIS environment. At present, we are developing an interface between a GIS and an EPA transport model for comparing our soil concentration maps with the EPA foreseen ground-level concentration maps from a punctual source. The final goal will be the optimization of the monitoring network, the localization of the zones, which need a more careful monitoring, and the optimal sites for chemical-physical monitors.

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