INDIRECT GEOSTATISTICAL METHODS TO ASSESS ENVIRONMENTAL POLLUTION BY HEAVY METALS. CASE STUDY: UKRAINE.

Carme Hervada-Sala[1], Eusebi Jarauta-Bragulat[2],
Yulian G. Tyutyunnik,[3] Oleg B. Blum [4]

1 Dept. Physics and Nuclear Engineering, EUETIT, Universitat Politècnica de Catalunya (UPC), Spain. Carme.Hervada@upc.es
2 Dept. Applied Mathematics III, ETSECCPB/EUETIB, Universitat Politècnica de Catalunya (UPC), Spain. Eusebi.Jarauta@upc.es
3 National University of Kyiv (Taras Shevchénko), Faculty of Geology, Kyiv, Ukraine. carme@univ.kiev.ua
4 National Botanical Garden, National Academy of Sciences of Ukraine, Kyiv, Ukraine. blum@cbg.freenet.kiev.ua

ABSTRACT

Environmental pollution by heavy metals is a red-hot issue. It is being studied from many points of view, as it is not only an environmental problem but also a public health matter. The effect of pollution by heavy metals can be assessed directly, that is measuring heavy metal concentration in soils, or using indirect methods, that is measuring heavy metal contents on living beings of regional ecosystem, in particular on plants. One of the organisms that have proved to be the most faithfully and useful to do so are moss. So, taking moss samples and measuring their heavy metal contents, we can study heavy metal environmental pollution.

The aim of this work is to show the use of geostatistical tools in environmental pollution analysis applied to a case study of environmental pollution by heavy metals in Ukraine (Polissia zone: Rivne , Zhytomyr, Kyiv and Chernigiv regions). To do so, two different information in that zone are available: on one hand, measures of heavy metal concentration in moss samples, whose location points are known. On the other hand, situation of polluting sites (industrial areas and towns) and their classification taking into account their polluting capacity. This information allows assessing not only for the regional pollution, but also for its scattering. From this and using geostatistical tools, sampling network is being improved. Data set consists of 80 sample points where concentration of ten elements (As, Cd, Cr, Cu, Hg, Fe, Ni, Pb, V and Zn) is measured. For each of them classical statistical analysis is done. Furthermore, spatial variability is studied using a new methodology based on Fast Fourier Transform (FFT), which allows finding covariance matrix using all variables at the same time. FFT methodology improves the classical and tedious geostatistical methodology based on variogram and cross-variogram modelling to find data spatial variability. Finally, contour maps of environmental pollution by heavy metals in studied area are presented and discussed.

Introduction and objectives

As it is well known, the increasing of industrial activities implies a pollutant impact on the environment. But, as our society demands, this technical progress associated with industrial activities must be compatible with quality of life technical progress, without renouncing to it. One of the most important contributions the environment pollution caused by industry is the presence of heavy metals in the air, which fall down when it rains and then are incorporated by leaving beings. Accumulation of heavy metals over large areas and long periods causes damage to living organisms and it must be carefully controlled; it is also important to know the effects of these contaminants. To assess the pollution caused by metals there are two different methods: the direct one, which consists of measuring their concentration in the air or in soil, and the indirect one, which consists of studying their presence in some living beings. If previous monitoring is correctly done, indirect method can be useful in environmental assessment, because it is easiest and cheapest.

In this article the presence of heavy metals from industrial origin in the Polissia region, located in the north of Ukraine, is studied, using analysis of moss samples taken in that region. The metals that are measured are: cadmium, chromium, copper, iron, mercury, nickel, lead, vanadium and zinc, and also the metalloid arsenic. Samples have been taken in the moss *Pleurozium schreberi*. The aim of this work is to build up contouring level maps of pollution by heavy metals using geostatistical methods; to do so, we take into account measures in several moss samples. The method used is kriging on a regular grid with correlogram tables obtained by applying the Fast Fourier Transform methodology (Yao, T. and A.G. Journel (1998)), once data have been transformed according the corresponding methodology in compositional data analysis.

Dataset description and analysis

Located in southeast Europe, Ukraine consists largely of fertile black soil steppes. Drained by the Dnieper, the Dniester, the Buh, and the Donets rivers, its area is about 601000 km^2 wide, extending from the Carpathians and the Volhynian-Podolian uplands in the west to the Donets Ridge in the southeast. The Dnieper divides the republic into right-bank and left bank Ukraine. In the north and northwest of the country is the wooded area of the Pripyat Marshes, with gray podzol soil and numerous swamps; wooded steppes extend across central Ukraine; and a fertile, treeless, grassy, black-earth (chernozem) steppe covers the south. The continental climate of the republic is greatly modified by proximity to the Black Sea. Ukraine is bordered by Belarus on the north, by Russia on the north, northeast, and east, by the Sea of Azov and the Black Sea on the south, by Moldova and Romania on the southwest, and by Hungary, Slovakia, and Poland on the west. Ukraine's population is about 48 million people; Kiyv is the capital and largest city. Administratively, Ukraine is divided into 24 oblasts, two municipalities with oblast status (Kiev and Sevastopol), and one autonomous republic (Crimea). In Figure 1, are represented maps of Europe and Ukraine.

Sampling was carried out in 1995 (April-July) on a quasi-regular grid of 32x32km. The data set consists of 79 samples of concentration (mg/kg = ppm) of 10 different elements in moss samples, with the coordinates of sample location (X=easting, Y=northing). The full data set can be found in our website. Those elements are: As, Cd, Cr, Cu, Hg, Fe, Ni, Pb, V and Zn. In Figure 2, is represented the scatterplot of sample location. In Table 1 is represented the descriptive statistics of sample variables; in table 2, are represented the covariance matrix and correlation coefficients matrix. In our website you can have a file with the histograms of data variables.

Figure 1.- Europe and Ukraine maps.

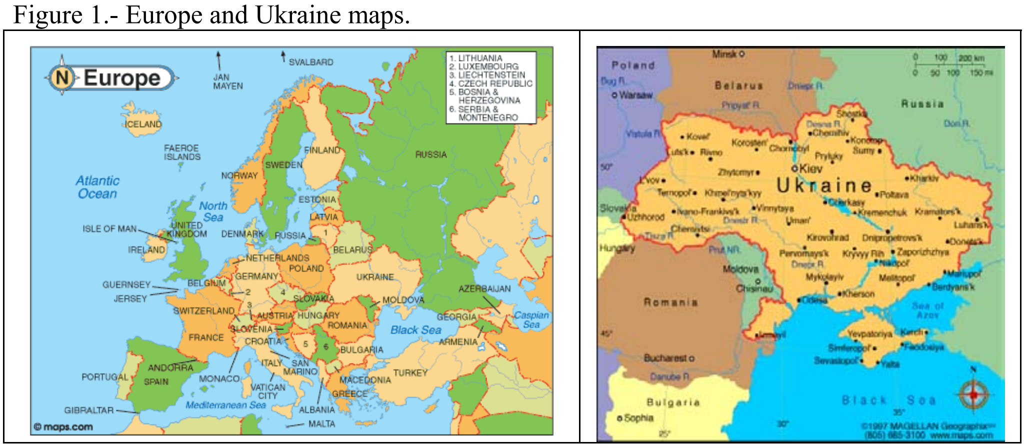


Figure 2.- Map of data locations.

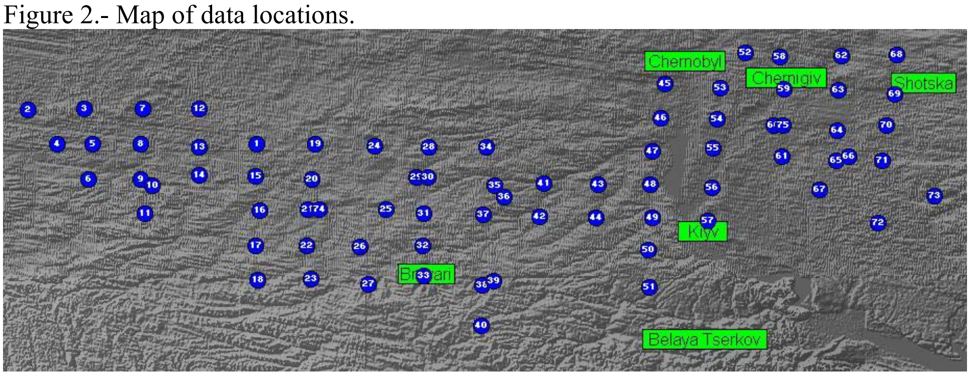


Table 1.- Descriptive statistics of data values.

	As	Cd	Cr	Cu	Hg	Fe	Ni	Pb	V	Zn
Mean	0,19080	0,19634	2,40741	8,00171	0,06450	385,42	2,77405	3,95424	1,95310	36,30443
Geometric mean	0,11705	0,18904	1,91248	7,01427	0,06132	349,98	2,44878	3,68765	1,69985	32,33085
Median	0,10500	0,19000	1,72500	6,05000	0,06000	335,00	2,62000	3,50000	1,80000	30,00000
Mode	0,06000	0,15000	1,70000	4,60000	0,05000	237,00	2,60000	2,20000	0,80000	30,00000
Standard dev.	0,22075	0,05717	1,59061	4,93148	0,02089	197,47	1,32461	1,55902	1,04166	20,53308
Variance	0,04873	0,00327	2,53003	24,31952	0,00044	38994,50	1,75460	2,43056	1,08505	421,60745
Kurtosis	7,07136	4,25432	0,14025	3,27205	1,27333	4,12	0,29704	1,31409	2,30765	6,01538
Symmetry	2,52315	1,45594	0,92887	1,97644	0,90613	2,02	0,63832	1,16654	1,24695	2,19910
Range	1,18200	0,34000	6,60000	21,50000	0,11500	920,00	6,03000	7,60000	5,50000	113,00000
Minimum	0,01300	0,08000	0,40000	3,20000	0,02000	159,00	0,70000	1,30000	0,40000	15,00000
Maximum	1,19500	0,42000	7,00000	24,70000	0,13500	1079,00	6,73000	8,90000	5,90000	128,00000

Geostatistical analysis: pollution maps

As data are concentrations in mg/kg (that is, ppm), we have to transform them to avoid the problem of the constant sum constraint (Egozcue and others (2003)). After our previous work (Jarauta and Hervada (2003) and Jarauta and others (2003)) we have chosen isometric logratio transformation (ILR) as the most suitable one. So, the first step in the geostatistical study, which is the most important goal of this work, is to transform our dataset into ILR-data. Then, the second step is to calculate the data Normal Score Transform (NSCT), according to the GSLIB procedure (Yao, T. and A.G. Journel (1998)).

Table 2. (a) Covariances and (b) Correlation coefficients of data values.

(a)

	As	Cd	Cr	Cu	Hg	Fe	Ni	Pb	V	Zn
As	0,0481									
Cd	0,0003	0,0032								
Cr	0,0786	0,0328	2,4980							
Cu	0,0742	0,0949	5,1000	24,012						
Hg	0,0011	0,0004	0,0177	0,0557	0,0004					
Fe	12,648	2,1652	114,76	-43,309	1,4928	38500,9				
Ni	-0,0193	0,0009	-0,1447	0,0834	-0,0044	2,8112	1,7324			
Pb	0,0454	0,0585	1,5157	3,8664	0,0190	128,0	-0,0860	2,3998		
V	0,0219	0,0007	-0,0966	-1,3651	0,0074	62,8	-0,2864	0,2623	1,0713	
Zn	-0,4410	-0,1030	-3,5541	5,7946	0,0092	325,7	8,1025	-0,4540	-1,0550	416,3

(b)

	As	Cd	Cr	Cu	Hg	Fe	Ni	Pb	V	Zn
As	1,0000									
Cd	0,0277	1,0000								
Cr	0,2267	0,3655	1,0000							
Cu	0,0691	0,3408	0,6585	1,0000						
Hg	0,2346	0,3332	0,5398	0,5475	1,0000					
Fe	0,2939	0,1943	0,3700	-0,0450	0,3666	1,0000				
Ni	-0,0669	0,0124	-0,0695	0,0129	-0,1601	0,0109	1,0000			
Pb	0,1335	0,6649	0,6191	0,5093	0,5915	0,4213	-0,0422	1,0000		
V	0,0966	0,0113	-0,0590	-0,2692	0,3456	0,3092	-0,2102	0,1636	1,0000	
Zn	-0,0985	-0,0889	-0,1102	0,0580	0,0218	0,0813	0,3017	-0,0144	-0,0500	1,0000

The third step, which is the equivalent to calculate and model variograms in classical geostatistics, is the building of the initial correlogram matrix using Fast Fourier Transform (FFT) following the methodology established by Yao and Journel (1998) and Ma and Yao (2001). This matrix consists of a 11×11-block matrix, which has in its diagonal the auto-correlations and the remaining the cross-correlations. So, we obtain 66 different correlation maps. The number of grid points in each map has to be of $1+2^n$; in this case we have $n=4$, that is, we have a 17×17 element matrix. The correlations have been interpolated using a size 10 smooth window and then multismoothing using all correlations and variables with size 3 maximum half window has been carried out to have the final correlation. Some of those 66 maps are hanged at our website.

The fourth step is to krige on a regular grid using those correlation maps. Kriging has been done using the program KB2D modified by Hervada-Sala and Jarauta-Bragulat (2001). After kriging, coordinates must be added taking in mind grid parameters. Then, back transformations of all results must be computed to recover ILR space. The last step consists of back transforming ILR interpolated values to recover original data space, and draw the corresponding contour maps. Figure 3 shows the contour maps obtained from the kriging grid with the right back transformed values.

Conclusions

The main conclusions of this work are:

1. The most interesting fact is Cu distribution. The high concentration of Cu in the west zone of studied area means that the most important factor in Cu concentration is the existence of enriched in Cu sandstone. It seems that wind is the responsible for copper pollution on moss.

2. Elements Cr, Pb and Zn are related to copper sandstone, too, as it can be seen in their higher concentrations in the same region.

3. In that regional scale it is not possible to see the effect of traffic on roads, the main factor for lead concentration.

4. The man made Hg, there are some chemical factories in the area, migrates in atmosphere as a gas and its distribution is very affected by weather. This is clearly shown by the maps.

5. Concentration of element V is very high around the thermal centrals that burn crude oil.

6. Element Zn is found near chemical factories (hog gum and plastic) in Chernigiv and Belaya Tserkov. The third point belongs to a zone near Shotska, which is out of the scope of this study, but this reveals the importance of weather factors in the concentration of Zn.

7. The central anomalies in Cr and Fe are related to engine factories in Kiyv and Brovari.

8. High concentration in As can be related to tanning and home chemical making.

9. The north concentration of Cd and Pb can be due to old machinery disposed after Chernobil accident.

References

Deutsch, C.V. and A.G. Journel (1998). Geostatistical software library and user's guide – GSLIB. Oxford University Press, 1 CD + 369 pp.

Egozcue, J.J., V. Pawlowsky-Glahn, G. Mateu-Figueras and C. Barceló-Vidal (2003). Isometric logratio transformations for compositional data analysis. Mathematical Geology, vol.35.

Hervada-Sala, C. and E.Jarauta-Bragulat (2001). Modifications to kb2d program in GSLIB to allow use of tabulated covariances calculated with Fast Fourier Transform method. Computers & Geosciences, vol.27, num. 07, pp 887-889.

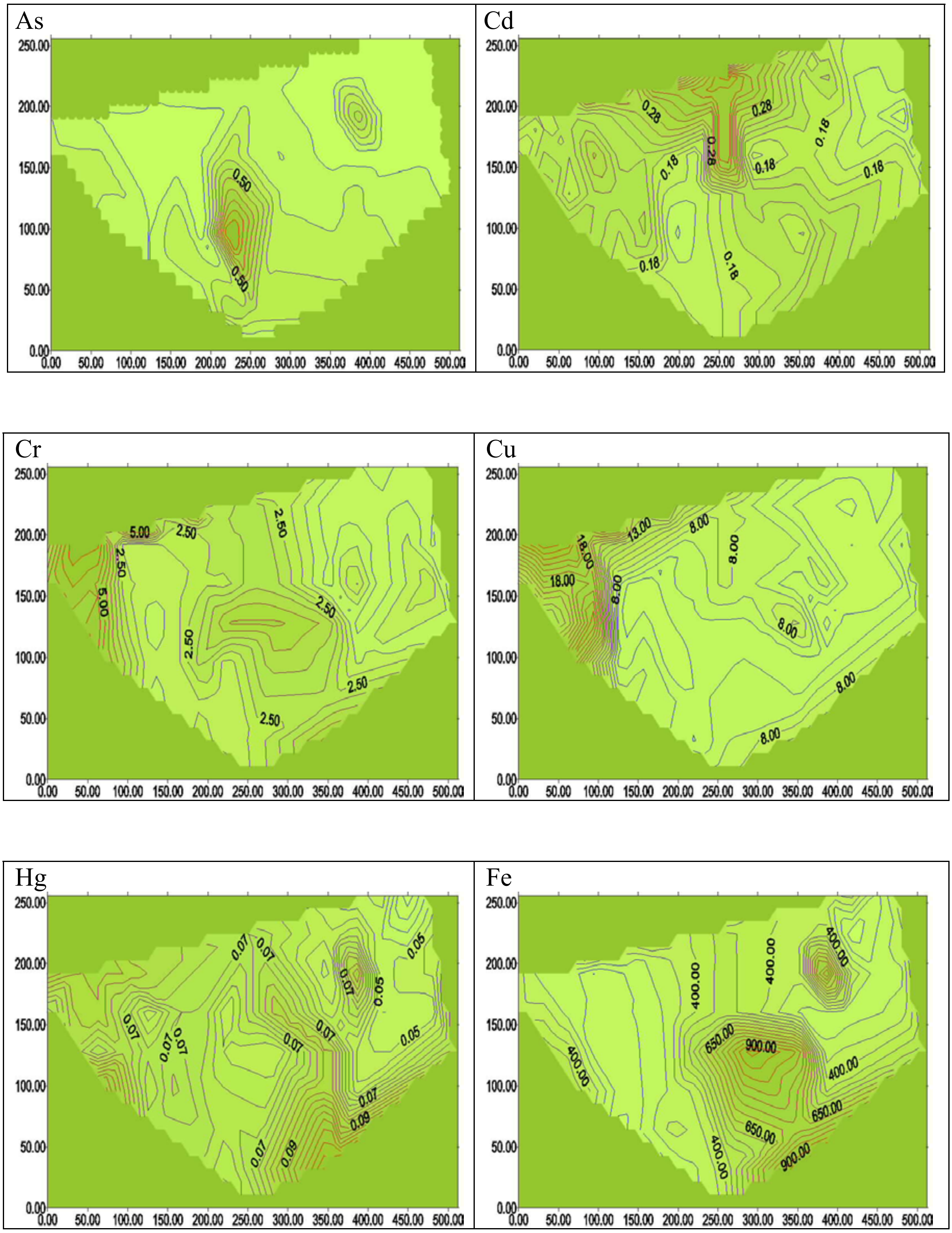
Jarauta-Bragulat, E. and C. Hervada-Sala. Comparison of kriging results of regionalized compositional data using three different data transformations. Case study: bauxites in Hungary. Submitted for presentation in IAMG'2003.

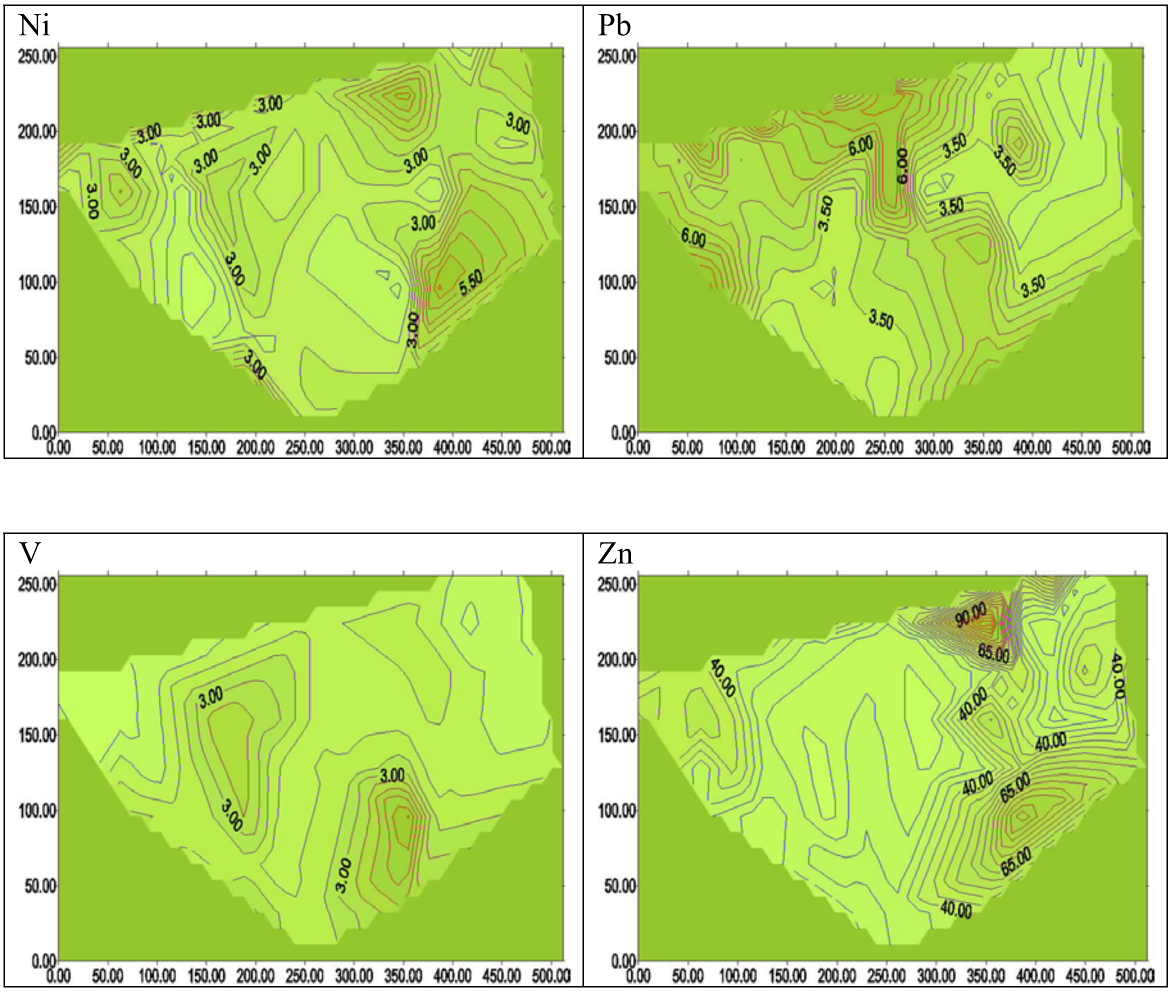
Jarauta-Bragulat, E, P. Buenestado-Caballero and C. Hervada-Sala. An algebraic method to compute isometric logratio transformation and back transformation of compositional data. Submitted for presentation in IAMG'2003.

Ma, X and Yao,T. (2001). A program for 2D modeling (cross)correlogram tables using Fast Fourier Transform. Computers & Geosciences, vol.27, num. 07, pp 763-774.

Yao, T. and A.G. Journel (1998). Automatic modelling of (cross)covariance tables using fast Fourier transform. Mathematical Geology, 30(6), 589–615.

Figure 3 - Contour maps of the ten studied elements





Acknowledgements.

Authors want to thank specially: the Department of Applied Mathematics III (UPC), the School of Civil Engineering (UPC) and the "Consorci Escola Industrial de Barcelona" (CEIB), for its support in this contribution.