GEOSTATISTICAL STUDY OF CONTAMINATED LAND IN WIRKSWORTH, DERBYSHIRE - ENGLAND

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Summary

The problem of pollutions and contamination of environments is an actual and important, moreover that for the last 35 years the quality of environment in some high industrial developed countries change for the worse. The polutions and contamination have different origin: domestic: agricultural, industrial, or commerce and transportation waste. From other side environment regenerates itself by geochemical and geophysical processes as dispersion, oxidative degradation-mineralization, anaerobic degradation etc. Importatnt part of recreation activities is to be known the origin and space distribution of the polutiants and quantity of contaminated soils to be removed. The site choosen for Geostatistical study has several peculiarities: - substantial concentration of heavy metals at the site, in 1300-1550 AD in this area was exist lead smelting artisan; - there are no processes cause short term variation of the metal concentration; - no agricultural activity since 1948; - dimensions are typical of investigations of contaminated land. The studied area has an irregular shape and maximal size of 165 m in NE direction and 190 m in SE direction, was located near the town of Wirksworth, Derbyshire in the English Midlands. The topsoil was sampled by three different sampling (Simple Regular - 40 samples, Herringbone design - 39 samples, with alteration 5m offset and Stratified Random design - 39 samples) protocols up to 15 cm deep with diameter of the samples of 2.5 cm. Two variables Barium (***Ba***), and Cadmium (***Cd***), subject of the study was analyzed using ICP-AES method. The main objectives of this study are to be estimated the space relation between Barium (***Ba***) and Cadmium (***Cd***), and their distribution and concentration in the area. Also we point to determine the bias and the best sampling design protocol. Barium's (***Ba***) concentration are between 345 and 3070 µg/g, in one normal distribution and with low variability and coefficient of variation = 0.37. The concentrations of cadmium (***Cd***) varied in wide interval (0.5-32.0 µg/g) in two mixed lognormal distributions: 0.5-1.5 µg/g, caused by natural variability, and 1.9-32.0 µg/g (with probability, p=0.80), caused by human activity (lead smelting artisan in 1300 - 1550 AD, and the coefficient of variation is = 0.79. Estimation of the values for barium (***Ba***) (in blocks 20 m by 20 m) performed with Ordinary and Universal Kriging procedure give us two very similar estimations of concentrations. The second one is more omtimistic (extended outside of studied area). Estimation of the values for cadmium (***Cd***) (in blocks 20 m by 20 m) performed with Ordinary Kriging procedure show high concentration which are located in the central part of the studied area into two local places, which containes all outliers, (***Cd*** > 13 µg/g). The best sampling design protocol for barium (***Ba***) is a Simple Regular one. All Geostatistical calculation were made by ISATIS™. ISATIS™ is a trade mark of GEOVARIANCES.

Introduction

Now one of the most actual and important problem is this one of the pollutions and contamination of environments. So for example according the data of National Center for Economical Alternatives (NCEA), Washington, D.C., U.SA. wrote (Standart, 11 April 1995, p. 9) for last 25 years the quality of environment in some high industrial developed countries change for the worse as a follows:

FRANCE	*- 41.2%*
CANADA	*- 38.1%*
U.S.A.	*- 22.1%*
… … … …	
DENMARK	*- 10.6%.*

The situation will be more serious (NCEA), if the economical grown up during this period will be highest. Some years ago more of the high industrial developed countries accept a series of new laws and correct existing this for protection of environments. However, independently of this and of the obligations taken from the governments of this countries, that they will controlled this processes, the general tendencies are anxiety.

The problem of pollution and contamination is important and actual. Fairbridge (1972, p. 310) distinguish different types of pollution: biological; chemical (organic and inorganic); physical. Their have different origin: domestic: agricultural, industrial, or commerce and transportation waste. Geochemical and geophysical processes by which the environment regenerates itself are;

dispersion, oxidative degradation-mineralization, anaerobic degradation.

I. The data and the aims of the study

The data were kindly given by Ariadni Argyraki and Dr. Michael Ramsey from Department of Geology, Imperial College, London (UK SW7 2BP).

1. Location of studied area, variables. Sampling design protocols. Support of the variables

Location

The studied area was located near the town of Wirksworth, Derbyshire in the English Midlands (Fig. 1.1.). The maximal size of the area is 165m in NE direction and 190 m in SE direction. The shape of the area is irregular. This area was originally described by **(Maskall & Thornton 1993.)**, and chosen by **Ramsey Argyraki, & Thompson, 1995**, (Fig. 1. 1.), because of several reasons **(Ramsey, et al 1995)**:

1/ substantial concentration of heavy metals at the site, in 1300-1550 AD in this area was exist lead smelting artisan;

2/ there are no processes cause short term variation of the metal concentration;
3/ no agricultural activity since 1948;
4/ dimensions are typical of investigations of contaminated land;
5/ the intentions and activity of the owner.

Sampling design protocols
Three different sampling protocols were used: simple regular grid (R prot.), illustrated here and below by grade of barium (***Ba***), Fig. 1.2., herringbone design, Fig. 1.3.,

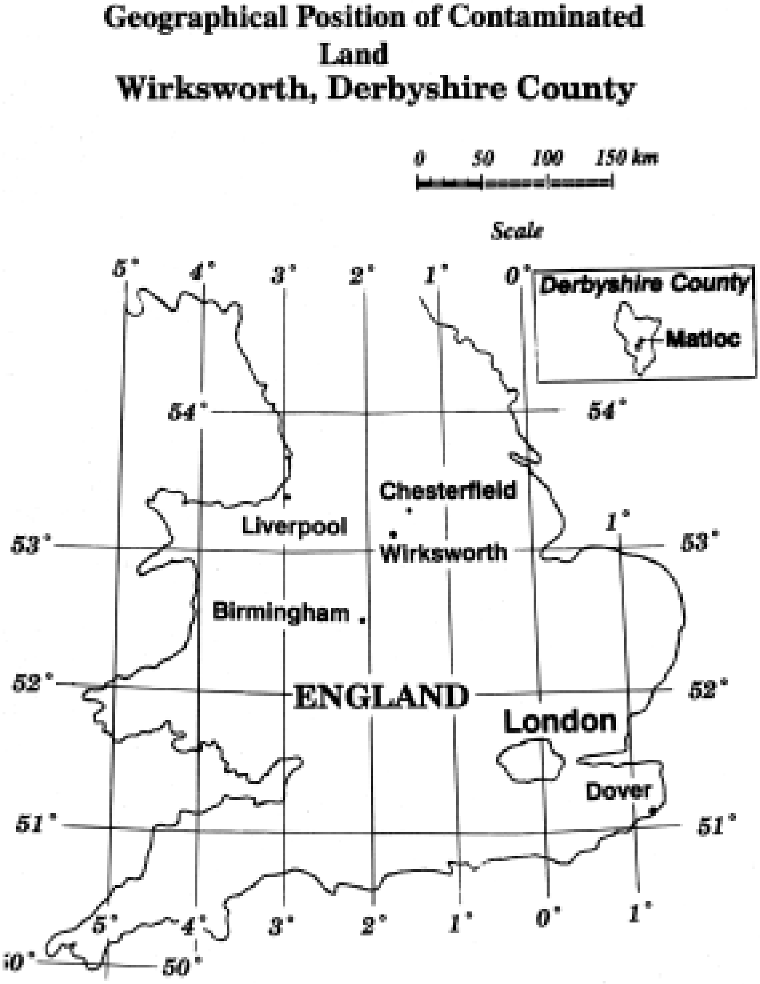

Fig. 1.1. Geographical position of contaminated land

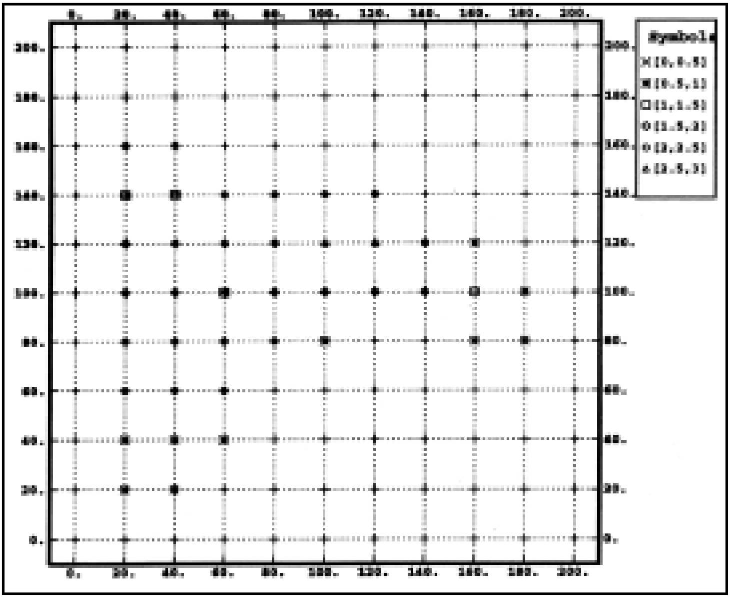

Fig. 1.2. Regular sampling protocol for barium, grid 20x20 m

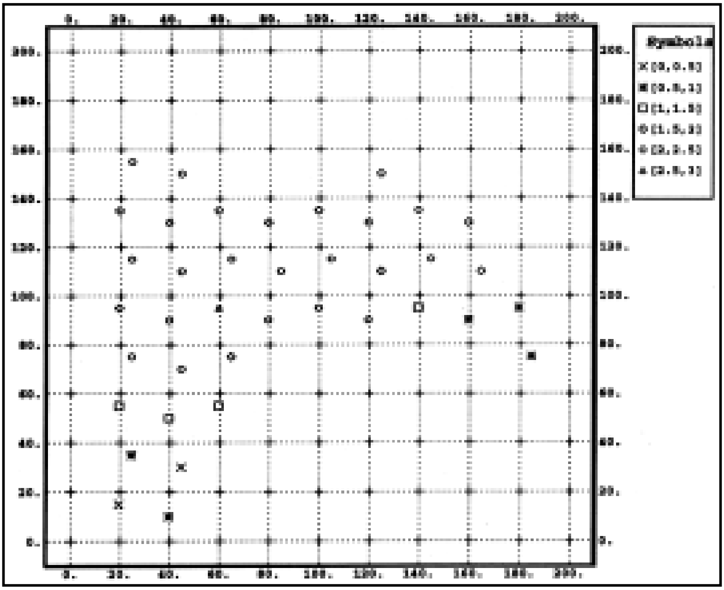

Fig. 1.3. Herringbone sampling protocol for barium, grid 20x20 m

Table 3.1. Estimates of Abundance (ppm) of Ba and Cd in the Lithosphere, after (Govett, (ed.) 1983, p. 19)

Atomic number	**Element**	**2:1 felsic/ mafic (Vinogra-dov, 1962)**	**1:1 granite/ basalt (Taylor, 1964) 1970)**	**Continen-tal Crust (Lee Tan &Yao Chi-lung,**	**Igneous Rocks (Horn & Adams, 1966)**
48	Cd	0.13	0.2	0.15	0.19
56	Ba	650	425	400	595

with alteration 5m offset the regular square grid (H prot.) and stratified random design, Fig. 1.4., (S prot.). The topsoil was sampled up to 15 cm deep with diameter of the samples of 2.5 cm **(Ramsey, et al. 1995).**

Variables
Two variables are subject of this study. Barium (***Ba***), and Cadmium (***Cd***). There were analyzed using ICP-AES, **(Ramsey, et al. 1995)**. Before this the samples were prepared using the common technology, decomposition with nitric and perchloric acids **(Ramsey, et al. 1995)**.

*Table 3.2. Cadmium in Granitic Rocks. Method in brackets, after (***Wedepohl, K. H. (ed.) 1978, p. 48-E-l***)*

##	**Material**	**Cd (ppm)**	**Author**
1	Granite, G-1, Rhode Island, U.S.A.	0.003 (P)	Wahler (1968)
2	Granite, G-1, Rhode Island, U.S.A.	0.05 (S)	Brooks etal.(1960)
3	Granite, Minnesota, U.S.A.	0.13(C)	Sandell & Goldich (1943)
4	Granite, Germany	0.2 (S)	Preuss (1940)
5	Ribeckite-granite, Afu Hill, N. Nigeria	1.56 (P)	Butler & Thompson (1967)
6	Quartz monzonitenite, unknown	1.4-1.8 (A)	Nakagawa & Harms (1968)
7	Granite, Germany	2(0	Champ (1968)

Table 3.3. Cadmium in Intermediate Rocks. Method in brackets, after (**Wedepohl, K. H. (ed.) 1978, p. 48-E-3**)

##	**Material**	**Cd (ppm)**	**Author**
1	Basalt ("Diabase"), W-1, Centerville, Va., U.S.A.	0.07,0.09 (S)	Brooks et al. (1960)
2	Basalt, Mt. Wellington, Tasmania	7(P)	Smythe & Gatehouse (1955)
3	Sienite, S-1, CAAS standard, Bancroft Area, Ontario, Canada	8(S)	Moxham (1967)

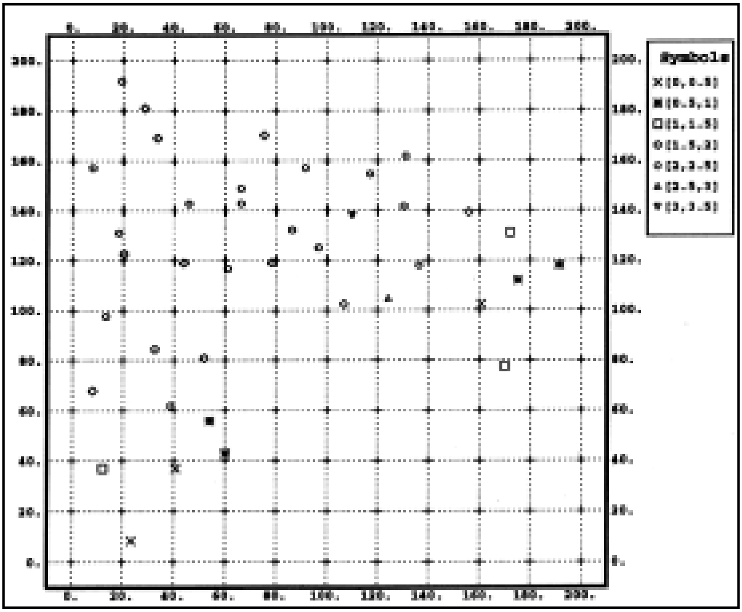

Fig. 1.4. Stratified random sampling protocol for barium, grid 20x20 m

Table 3.4. Cadmium in Sedimentary Rocks. Method in brackets, after (**Wedepohl, K. H. (ed.) 1978, p. 48-E-3**)

##	Material	Cd (ppm)	Author
1	Glass sand, NBS-81 standard	0.014 (A)	Wahler (1968)
2	Plastic clay, NBS-99 standard	0.016 (A)	Wahler (1968)
3	Bentonite, mostly Montana and S. Dacota, U.S.A. (10 samples)	0.3-11.0 (C)	Tortelot et al. (1955)
4	Bituminous Shale (Kupferschiegel) Mansfeld, Germany	500	Cissarz (1930)

Support of the variables

The support of the variables is as a follows: sampling of the topsoil up to 15 cm deep in three different sampling design protocols through the samples with diameter 2,5 cm.

2. The aims

The main objectives of this study are:

1/ To be estimated:
a/ the space relation between Barium and Cadmium;
b/ the distribution of Barium and Cadmium in the studied area
c/ the concentration of Barium and Cadmium.

2/ To be determined:
a/ the bias sampling design protocol;
b/ the best sampling design protocol.

Sampling procedures were performed in the same time and using one technic for all sampling design protocols Ramsey, M., (personal communication).

3. Chemistry and Geochemistry of Cadmium (***Cd***) and Barium (***Ba***)

Some integral data for distribution of cadmium and barium was shown in Table 3.1. The normal concentration for cadmium is between 0.13 and 0.2 ppm, and for barium they are in the interval of 400 and 650 ppm.

3. 1. Chemistry of cadmium (***Cd***)

Cadmium belonging to the group **IIB** of transition heavy metals (**Fairbridge, 1972, p. 406**) with element as zinc ($_{30}\boldsymbol{Zn}$) and mercury ($_{80}\boldsymbol{Hg}$).

3.2. Geochemistry of cadmium (***Cd***)

The abundance of cadmium for igneous (granitic and intermediate) and sedimentary rocks was shown in Table 3.2. - 3.4., consequently.

3. 3. Cadmium concentration range

Cadmium is recovered almost entirely as a by-product in the treatment of zinc-bearing ores (Wedepohl, K. H. (ed.) 1978, p. 48-0-1).

3.4. Chemistry of barium (***Ba***)

Barium ($_{56}\boldsymbol{Ba}$) belonging to the group IIA of light metals (Fairbridge, 1972, p. 406) together with elements as a beryllium ($_{4}\boldsymbol{Be}$), magnesium ($_{12}\boldsymbol{Mg}$), calcium ($_{20}\boldsymbol{Ca}$) and strontium ($_{38}\boldsymbol{Sr}$) and radium ($_{88}\boldsymbol{Ra}$). The extend of solid solution of barium is very limited (Krauskopf, K. B. 1967).

3.5. Geochemistry of barium (***Ba***)

Barium belonging to the group of trace elements (Mitchell, 1964). Some data about abundance and distribution of barium (***Ba***) in the Earth’s Crust after (Wedepohl, 1978) are illustrated in Table 3.5.

Table 3.5. Abundance of Ba in important masses of the earth's crust. (Means calculated on the basis of Wedepohl's 1969, data on the abundance of rock units)

Igneous intrusive rocks (mean)	**728 ppm**
Gabbroic rocks	246 ppm
Granites	732 ppm
Granodiorites & quartzdiorites	873 ppm
Diorites	714 ppm
Consolidated sediiments (mean)	**538 ppm**
Sandstones (inchad. graywakes)	316 ppm
Shales	628 ppm
Carbonate rocks	90 ppm
Sea water	**0.020 ppm**

Abundance of barium in sedimentary rocks (shales and carbonates) was shown in Table 3.6. and 3.7.

Table 3.6. Barium in shales from Great Britain

No. of samples	**Barium concentration range, ppm**	**Barium concentration mean, ppm**	**Method**	**References**
6	**330-1050**	**555**	**S**	**Nicholls & Loring (1962)**
27	**325-1280**	**723**	**S**	**Spencer (1966)**

Table 3.7. Barium in carbonate rocks from Great Britain

No. of samples	**Barium concentration range, ppm**	**Barium concentration mean, ppm**	**Method**	**References**
183	**<5-8000**	**220**	**S**	**Muir et. al. (1956)**

3.6. Barium concentration range

The range of barium concentration in Great Britain is very high in the rocks and varied from 5 to 8000 ppm, (See Table 3.7.). However this range is highest for the soils is between 10 and 10 000 ppm, Fig. 3.1. **(Mitchell, 1964)**.

II. Formalization of data and models

The formalization of the data is a usual procedure for manipulation of the data provide for correctness and coordination between the reality and the geological (respectively mathematical) model (Miller, Kahn, 1965).

Generally two models are necessary to be created. The first one is a geological (geochemical) model, which reflect our special knowledges on the nature of data and the second one - mathematical model, which should be modelled through geological one. It is obvious that the main model here is the first one - the geological model. In another words, if our geological model is not correct, we can not expect true results independent of this, which sophisticated mathematical procedures we have used **(Yordanov, M. A. 1992)**. This situation is very close to the similar one in the programing world "Garbage in, garbage out".

In this study distribution of the concentrations of cadmium and barium could be presented effectively with their geochemical anomalies, which are geological anomalies simultaneously. Further in the explanation we will use both of the names.

Some different definitions exist concerning the geological anomalies. We keep respect to one of them, provided by Bates, & Jackson (1987, p. 2) - "a geological feature ... which is different from the general surroundings and is often of potential economic value." Of course for our aim and set of data the end of previous quota should be changed to the next way," ... is often of potential environment value".

An interesting view of point concerning the location of anomalies in the space was given by Wackemagel, H. (personal communication in: Haslett, J., et al. (1991, p. 235.) "A geological anomaly of an interesting size should have an effect on several samples... What is looked for, is (often) one anomaly defined on a group of samples, none of these samples being necessarily an extreme value." In another words it is not necessary for anomalies to be presented just by extreme high values, they could exist as a portion of the space stipulated for extreme values. This portions could be identified like threshold in the geological space and in this way there are very close to the conceptions of threshold in geochemistry.

4. About the factors impacted the models

4.1. Configuration of the soil body be sampled

One of the mains geological factors affecting sampling is "the shape and the position in the ground" **Koch & Link (1970, p. 268)**. Formally the shape of the geochemical body may be tabular, and this class may be divided into two subclasses planar and folded. The planar may be horizontal and inclined (p. 269).

4.2. The influence of the scale of structure on the natural variability

Conditionally **Koch & Link (1970)** distinguished two types of structure, macro- and microstructure. The scale of structure of soil body may produce a different effect on the variability. So for example, macro- or microstructure may be dominant source of natural variability in microstructure or it may be small compared with the variability on the scale of the macrostructure.

5. Geochemical model

5.1. Variability of geochemical data. Original of natural variability. The problem of uniformity

According the general theory of statistic when we estimate the mean we have two possibilities to reduce the standard error of the mean:

1/ to reduce the variance;

2/ to increase the number of observation (Koch & Link, 1970). Even for us, is not possible to increase the number of observation, because the data set was final, the first option is available - reducing the variance. We will use this statistical characteristic often.

5.1.1. Components of variability in natural geochemical systems

The variability in geological (geochemical) systems was caused mainly of global and complicate processes in the earth's crust. However local areas with high contrasts properties are product by similar, but more complicate and different natural processes. Finally we obscure two types of environments in the space and time - background and anomalies, both of them which are product of natural variability.

Univariate observation — ***w*** is equal to:

(5.1.)
$$w = \mu + \chi_n + \chi_s + \chi_p + \chi_a + \varepsilon$$

where: μ - population mean

χ_ν - natural variability, property of rock (soil) bodies;

χ_σ - sampling variability;

χ_π - preparation variability;

χ_α - analytical variability;

ε - random fluctuation not accounted for by the other sources of variability.

5.1.2. Components of variability in mixed (natural & artificial) geochemical systems

(5.2.)
$$w = \mu + \chi_n + \chi_{ha} + \chi_s + \chi_p + \chi_a + \varepsilon$$

where: χ_{ha} - artificial variability, produced by human activity

5.1.3. Assumptions:

1. The sum of natural and artificial variability is great than the sum of: sampling, preparation and analytical variabilities

(5.3) $$(\chi_n + \chi_{ha}) > (\chi_s + \chi_p + \chi_a)$$

2. The sum of this previous variabilities is great than ε - random fluctuation (not accounted for by the other sources of variability)

(5.4.) $$(\chi_s + \chi_p + \chi_a) > \varepsilon$$

3. Preparation & analytical variabilities has not systematical errors

(5.5.) $$\chi_p > \varepsilon_p$$

(5.6.) $$\chi_a > \varepsilon_a$$

4. Or finaly all previuous relation could be presented as a follows:

(5.7.) $$(\chi_n + \chi_{ha}) > (\chi_s + \chi_p + \chi_a) > \varepsilon$$

5.2. Are the soils homogenous?

Generally the soils are not homogenous geochemical systems comparing with another one, because their are product of destruction of the rocks (usually more than one) by hypergenetic processes. The level of biological and human activity is very high also. So finally we may consider soils as a very mobile geochemical systems with high dynamic of exchanging of products and heterogeneity.

This heterogeneity of the soils is an important fact from geostatistical point of view because of the strong influence of the space distribution of regionalized variables.

Independently of this we may identify areas in the soils, in appropriate scale (Koch & Link 1970), with lowest heterogeneity, and to assumed them as a homogenous (more or less).

6. Mathematical model

Geostatistical Approach

6.1. Natural & artificial geochemical variability as a main subject treated in terms of geostatistics

(6.1.) $$(\chi_n + \chi_{ha}) \Leftrightarrow Geostatistical\ Variable$$

7. The model

7.1. Orientation of the area in the space

The NE direction of the grid is rotated in 74° clockwise. This direction was called conditionally Y direction. Respectively the orthogonal one (SB's direction) was called X direction.

7.2. Dimension of the space

We considered the model into 2D, because along the third axis Z, the size is insignificant small (just 15 cm), comparing with the size of area along X and Z axis So, further we will work with plane (XOY).

7.3. Shape of the area and it position in the space

Shape of the area is quite irregular along the axis X and Y. The area was inclined to SW direction approximately in 6°.

7.4. Nature of geochemical variability of cadmium and barium

Geochemical variability of cadmium and barium was mixed product constructed by two components: natural variability and variability produced by human activity. This two components formed in 2D space conditionally homogenous geochemical space.

7.5. Geochemical variability of cadmium and barium in terms ofgeostatistics

Geochemical variability of cadmium and barium may be considered in the terms of geostatistics as a regionalized variables.

Summarize all previous we may consider the model as a:

Inclined in 6° along Y axis (to SW direction), planar, homogenous soil body, in 2D space (XOY plane), with quite irregular shape, and mixed nature of geochemical variability of cadmium and barium interpreted in the terms of geostatistics as regionalized variables. This regionalized variables was studied in three different sets of data (regular, herringbone and stratified random design sampling protocols) and one common, integral set, called all protocols.

The base map for barium (**Ba**), all sampling protocols was shown on Fig. 7.1. Using this model we will try to apply the geostatistical tools for local estimation of cadmium (**Cd**) and barium (**Ba**) grade in the studied area. This task is very similar to local estimation above the cut-off grade, especially for cadmium.
So far as in the grade of cadmium (Cd) is with high variability the more important task will be to identify the zones with abnormal high grade.

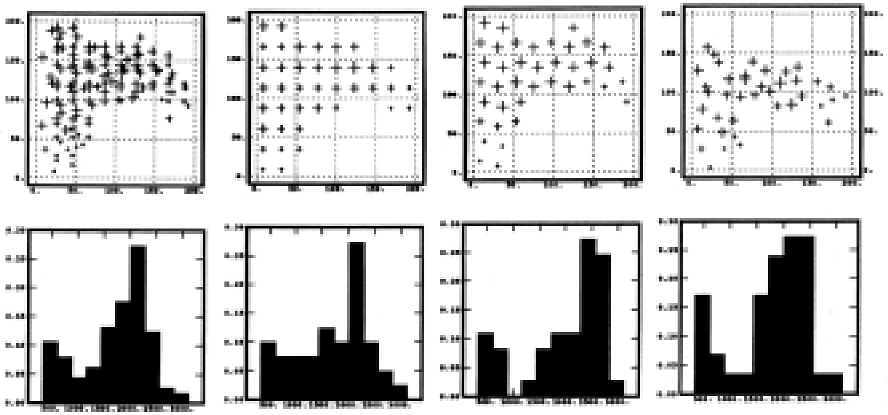

Fig. 7.1. The histograms for barium, all sampling protocols

However the barium (Ba) grade lie between typical limits for the trace elements in the soils. Just the zones with relative high grades may be important, if we accept the hypothesis that it is connected (statistically significantly) with cadmium.

III. Geostatistical Methods

8. Basic statistical characteristics

The input data are graphically presented by the base map (proportional). Correct using of the data oblige the procedure to check for duplicate points. This checking was realized at minimum distance equal to 0.10 m. No indication for duplicate points in regular, herringbone and stratified random sampling protocol and in all sampling protocols.

8.1. Mean, variance, standard deviation, coefficient of variation

This statistical parameters was calculated by trivial formulas explaining below (8.1.1.-8.1.4.), and summarized in Table 8.1. and 8.2. The coefficient of variation for cadmium and barium for three different sampling protocols and all protocols was shown on Fig. 8.1. and Fig. 8.2.

8.1.1. The mean - $\overline{X}$

$$Mean = \frac{1}{N}\sum_{i=1}^{i=n} X_i$$

where: X_i - the current value of the variable;
N - the number of observations in the population.

Table 8.1. Summary Statistics of ***Cd*** *concentration (original values), for regular, herringbone, and stratified protocol and for all protocols*

Statistics	Regular design sampling protocol	Herringbone design sampling protocol	Stratified design sampling protocol	**Grand mean** (all design sampling protocols)
Minimum, μg/g	0.5	1	1	0.5
Maximum, μg/g	17.3	32	13.5	32
Mean, μg/g	4.626	5.494	4.332	4.816
Standard dev.	3.053	5.016	2.796	3.782
Coefficient of variation	0.66	0.91	0.65	0.79
No. of observ.	40	39	39	118

Table 8.2. Summary Statistics of ***Ba*** *concentration (original values, for regular, herringbone, and stratified protocol and for all protocols*

Statistics	Regular design sampling protocol	Herringbone design sampling protocol	Stratified design sampling protocol	**Grand mean** (all design sampling protocols)
Minimum, μg/g	397	345	364	345
Maximum, μg/g	2910	2610	3070	3070
Mean, μg/g	1642.47	1711.79	1771.21	1707.93
Standard dev.	615.23	621.88	667.97	637.48
Coefficient of variation	0.37	0.36	0.38	0.37
No. of observ.	40	39	39	118

8.1.2. Variance - *Var*

$$Var = \frac{1}{N}\sum_{i=1}^{i=n}\left(X_i - \overline{X}\right)^2$$

where: $\overline{X}$ - the mean value of the population.

8.1.3. Standard deviation - *S*

$$S = \sqrt{\frac{1}{N}\sum_{i=1}^{i=n}\left(X_i - \overline{X}\right)^2}$$

8.1.4. Coefficient of variation - *V*

$$V = \frac{S}{\overline{X}} = \frac{\sqrt{\frac{1}{N}\sum_{i=1}^{i=n}\left(X_i - \overline{X}\right)^2}}{\frac{1}{N}\sum_{i=1}^{i=n} X_i}$$

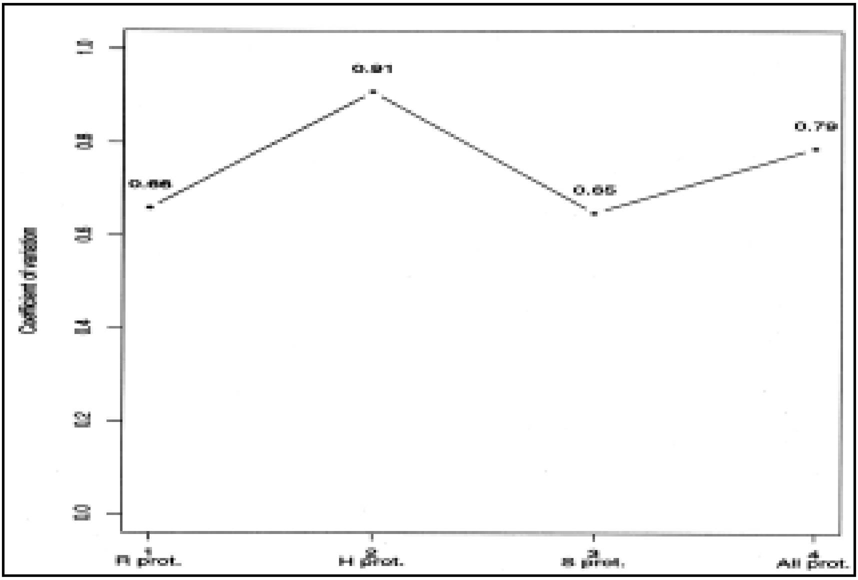

Fig. 8.1. Coefficient of variation for cadmium, R, H, SR and all sampling protocols

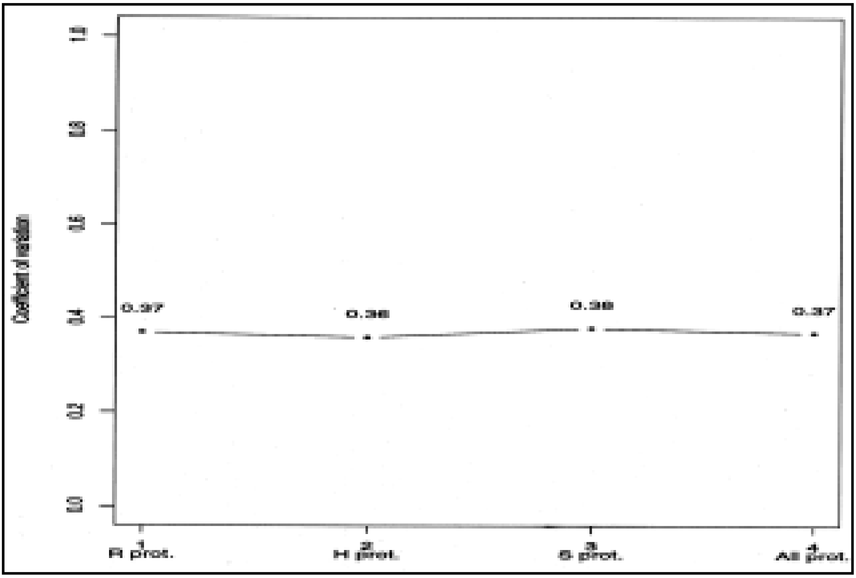

Fig. 8.2. Coefficient of variation for barium, R, H, SR and all sampling protocols

Important circumstance here is that coefficient of variability for barium is practically with the same values (0.37) in different sampling design protocols. This mines that barium is very well and homogenously distributed in the studied area.

8.2. Type of distribution of data

The distribution for cadmium and barium, raw data, was checked through building of histograms and performing of some statistical test cheeking the type of distribution and homogeneity of distribution as a GAPTEST **(Miesch, A. T. 1981)**.

Histograms was produced for cadmium (***Cd***) and barium (***Ba***) with different number of classes, depending of:

a/ number of observations, Sterjes's formula,

(8.1.)

$$d = \frac{(x_{\max} - x_{\min})}{(1 + 3.332 \lg(n))}$$

where: $x_{\max}$ - the maximum value of the variable;
$X_{\min}$ - the minimum value of the variable;
n - number of variables.

b/ value of standard deviation - *S*

(8.2.)

$$S = \sqrt{\frac{1}{N}\sum_{i=1}^{i=n}\left(X_i - \overline{X}\right)^2}$$

The width of the class intervals in the second case must be between $\frac{1}{4}$ and $\frac{1}{2}$ of the value of standard deviation, (Shaw, 1964).

8.2.1. Distribution of cadmium (*Cd*)

The histogram of cadmium was building for 10 classes and shown on Fig. 8. 3. - 8. 6. The homogeneity and the type of distribution was checked by *GAPTEST* program, (Miesch, A. T. 1981). For regular, herringbone and stratified random protocols, the skew is equal to 1.99, 3.96 and 1.32 consequently, which lead to the positive lognormal type distribution of data (see also Fig. 1., page 56 and Fig. 2., page 57).

Statistically significant gap with probability p=0.90 exist for the set of data 'all sampling protocols', where the skew is equal to 3.708 (searched the entire rang) and the gap is between 1.5 mg/g and 1.9 mg/g (see Fig. 1., page 56).

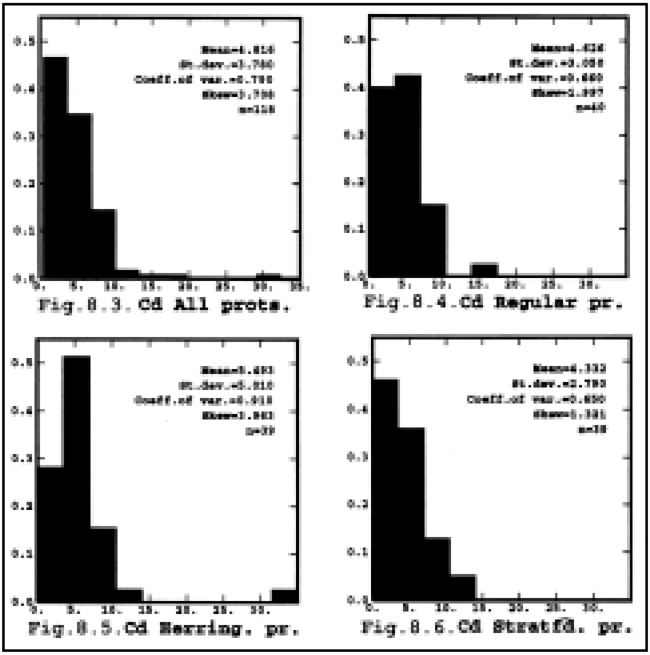

Fig.8.3. Cd All prots.

Fig.8.4.Cd Regular pr.

Fig.8.5.Cd Herring. pr.

Fig.8.6.Cd Stratfd. pr.

Fig. 8.3. - 8.6. Histograms and basic statistical parameters for cadmium, all sampling protocols, R, H and SR

8.2.2. Distribution of barium (***Ba***)

The barium histograms for 10 classes was shown on Fig. 8.7. - 8.10. The distributions for herringbone and stratified random protocol and for all sampling protocols is homogenous, i.e. without statistically significant gaps. A weakly negative lognormality exist for herringbone and stratified random sampling protocol and for all sampling protocols, the skew is equal to -0.925, - 0.718 and - 0.63 consequently.

For regular design sampling protocol, where the skew is equal to - 0.0351, (Fig. 8. 9.), appear a statistically significant gap with probability p=0.80 between 996 mg/g and 1320 mg/g.

8.3. Correlation between cadmium ***(Cd)*** and barium ***(Ba)***

Coefficient of correlation varied for different sampling protocol from 0.1922 (herringbone design sampling protocol) to 0.5563 (stratified random protocol), Fig. 8. 11. and Table 8. 3.

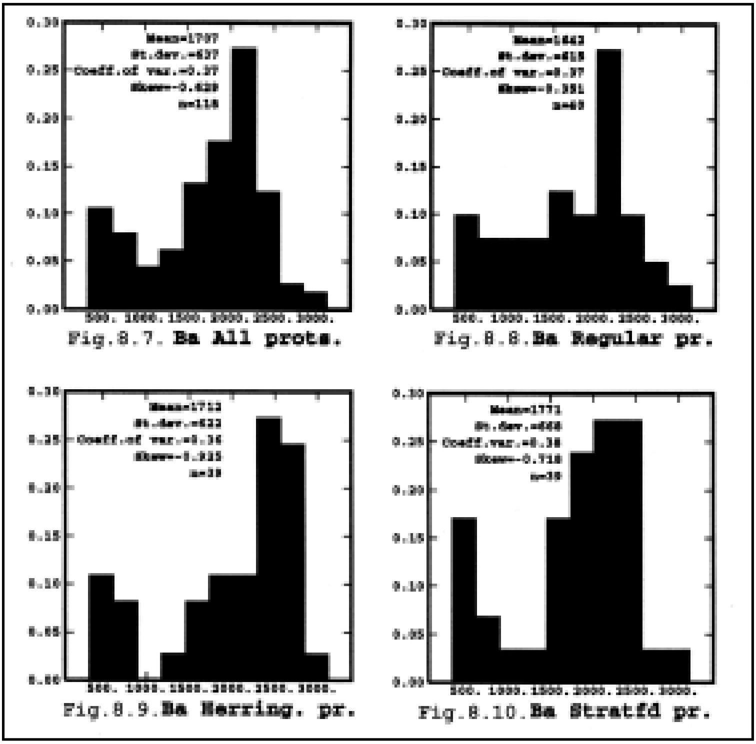

Fig.8.7. **Ba All prots.**

Fig.8.8.**Ba Regular pr.**

Fig.8.9.**Ba Herring. pr.**

Fig.8.10.**Ba Stratfd pr.**

Fig. 8.7. - 8.10. Histograms and basic statistical parameters for barium, R, H, SR and all sampling protocols

Table 8.3. Coefficients of correlation between ***Cd*** *ond* ***Ba*** *in different design sampling protocols (regular, herringbone, and stratified random) and in all protocols. The statistically significant values, for degree of freedoms* ***f****= (n-2) and a = 0.01 of the coefficient of correlation was marked with asterisks - *, after:* ***(Solovov & Matveev, 1985, Addenda VII, p. 217)***

##	**Sampling design protocol**	**Coefficient of correlation**
1	Regular (40 points)	0.4937*
2	Herringbone (39 points)	0.1922
3	Stratified random (39 pts.)	0.5563**
4	All protocols (118 points)	0.3529***

*critical value is 0.403 for degree of freedoms /==(40—2) and a = 0.01;

**critical value is 0.403 for degree of freedoms /=(39-2) and a = 0.01;

***critical value is 0.192 for degree of freedoms /=(118—2) and a = 0.01.

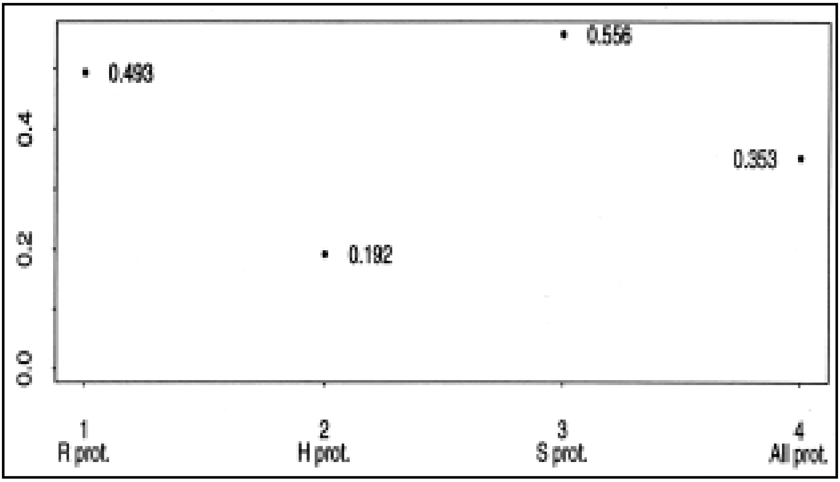

Fig. 8.11. Scatterplot of corelations between Ba and Cd for regular, heringbone and stratified random design sampling protocols and for all sampling protocols

The grades of concentrations of cadmium and barium was statistically significantly correlated for regular and stratified random design sampling protocols and for all sampling protocols.

9. The problem with outliers, extreme data and anomalies

9.1. About different type and influence of outliers on statistical and geostatistical estimations

An important part of any analysis of data is how to identify correctly the outliers. Haslett, J., et al. 1991, for more details see pp. 51-61.

9.2. Outliers for cadmium ***(Cd)***

Outliers for cadmium was estimated according the logic scheme (Table 1-3, pp. 52-53) and the detected in this way, was shown in Table 9.1., and Fig. 9. 1. - 9. 3.

Table 9.1. Outliers for ***Cd*** *, with values more than 13 µg/g*

##	**Outliers Parameter**	**1**	**2**	**3**	**4**
1	Cd, µg/g	32	17.3	13.5	13.0
2	X coor., m	20	80	12	105
3	Y coor., m	55	100	106	112
4	Sampling pr.	Hpr.	Rpr.	Spr.	Hpr.
5	Samples No	H13	R45	S6	H13

9.3. Outliers for barium ***(Ba)***

The are no outliers for barium detected by method proposed before.

10. Structural variogram analysis

10.1. Some theoretical aspects

Some theoretical aspects was discussed in Armstrong (1984) and Srivastava & Isaaks (1989).

10.2. Experimental variograms

10.2.1. Experimental variograms for Cadmium

The experimental variograms for cadmium was calculated in five standard directions: OMNI, 0°, 45°, 90" and 135° in the horizontal surface XOY, for numbers of lags equal to 6 and 8 with outliers was shown in Fig. 10.1 - 10.5.

Variograms calculated with lags equal to 8 and without outliers (See Table 9. 3. for 0° and 90° directions was shown in Fig. 10. 6. - 10. 8. Influence of outliers ## 1 and ## 2 was shown through variograms clouds in Fig. 4., page 58 (Cd = 32 mg/g) and in Fig. 5. page 59 (Cd = 17.3 mg/g).

Maximum distance - 82.5 m (120 m)
Tolerance - 22.5° (90° for OMNI)
Thickness of the slice = 241 m
Width of the slice = 50 m
Calculation lag = 15 m
Tolerance on distance = 7.5 m
Number of lags = 6 (8)
Variance of cadmium = 14.302 (with outliers)
Variance of cadmium = 5.458 (without outliers)

10.2.2. Experimental variograms for Barium

The experimental variogram models for OMNI directions, 0°, 45°, 90° and 135°, for all sampling protocols, regular, herringbone and stratified random protocols was produced with follows parameters:

Maximum distance - 82.5 m
Tolerance - 22.5° (90° forOMNI)
Thickness of the slice = 241 m
Width of the slice = 50 m
Calculation lag = 15 m
Tolerance on distance = 7.5 m
Number of lags = 6
Variance of barium = 406377

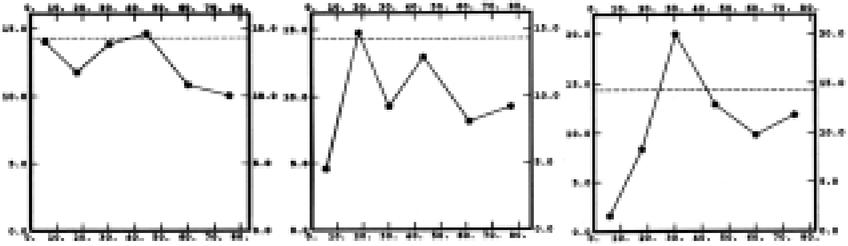

Fig.10.1. OMNI Fig.10.2. 0 degree Fig.10.3. 135 degree

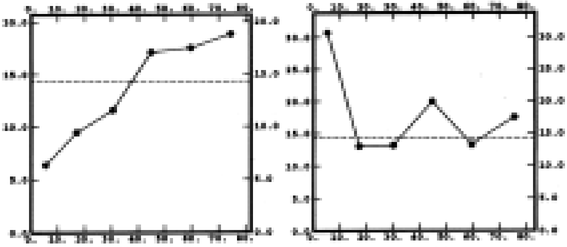

Fig.10.4. 45 degree Fig.10.5. 90 degree

Fig. 10.1 - 10.5. Experimental Variograms with outliers for cadmium for OMNI, 0°, 45°, 90° and 135° directions.

Experimental variograms was shown on Fig. 10.9 - 10.12. The variograms for 90° and 45° directions are unbounded, i.e. nonstationary, Fig. 10.10. and Fig. 10.11.

10.3. Variogram models

10.3.1. Variogram models for Cadmium

OMNI direction:

$$\gamma(h) = \begin{cases} 1.748 & h = 0 \\ 1.748 + 3.298\, sph(57.34) & 0 < h < 57.34 \\ 5.05 & h > 57.34 \end{cases}$$

Variogram for this direction was shown on Fig. 10. 13.

10.3.2. Variogram models for Barium

Three variogram was modelling, OMNI directions, 0° and 45°.
The variogram model for OMNI directions is as follows:

$$\gamma(h) = \begin{cases} 56200 & h = 0 \\ 56200 + 236000\, sph(63.13) & 0 < h < 63.13 \\ 292200 & h > 63.13 \end{cases}$$

Variogram for this direction was shown on Fig. 10. 14.

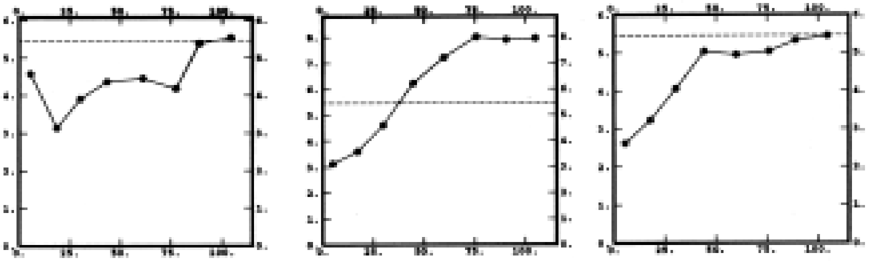

Fig.10.6. 0 degree Fig.10.7. 90 degree Fig.10.8. OMNI

Fig. 10.6 - 10.8. Experimental Variograms without outliers for cadmium for 0°, 90° and OMNI directions.

and for 0° direction

$$\gamma(h) = \begin{cases} 44600 & h = 0 \\ 44600 + 2900\, sph(17.07) + 247\, sph(82.42) & 0 < h \leq 17.07 \\ 47500 + 247000\, sph(82.42) & 17.07 < h \leq 82.42 \\ 294500 & h > 82.42 \end{cases}$$

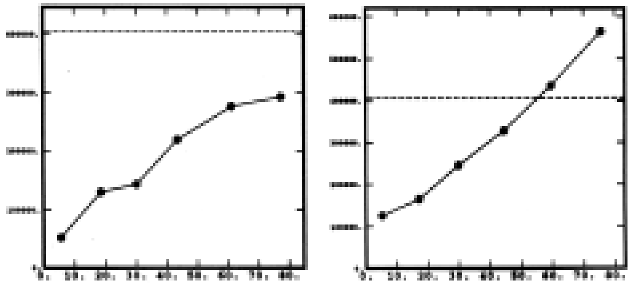

Fig.10.9.Ba (0) All pr. Fig.10.10.Ba (90) All pr.

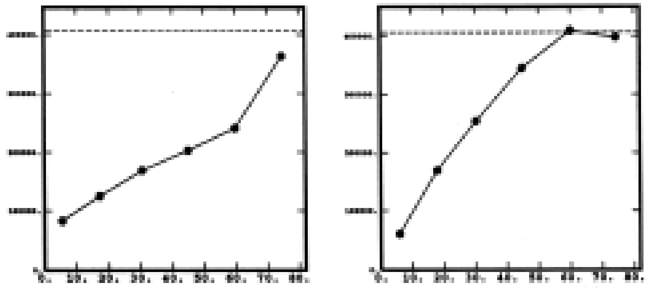

Fig.10.11.Ba (45) All pr. Fig.10.12.Ba (135) All pr.

Fig. 10.9 - 10.12. Experimental Variograms for barium for 0°, 90°, 45° and 135° directions.

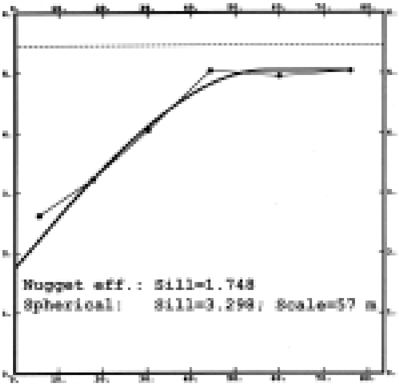

Fig. 10.13. Experimental and model variogram for Cd<12.9 µg/g, OMNI

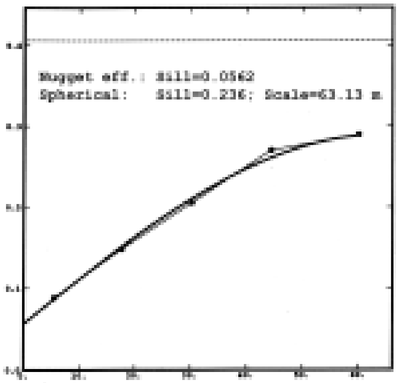

Fig. 10.14. Experimental and model variogram for Ba, OMNI

11. Neighborhood test

This test is the preliminary operation before the kriging estimation procedures intended to be applied. The omtimisation of the neighborhood distance was performed according two conditions, (Rivoirard, 1987a):

a/ the value of estimation krige variance must be minimum;
b/ the slope of regression must be close to 1.0.

11.1. Neighborhood test, cadmium ***(Cd)***

11.1.1. Moving neighborhood

This variant of neighborhood test was used in variant of angular sectors, according the follows parameters - Table 11.1.

Table 11.1. Parameters of neighborhood test for ***Cd****, the best size of the neighborhood was marked with asterisk - **

No	Min/OpL/Max	Number of Angular Sectors	XandY radius, (m)
1	3/24/32	8	20
2	3/24/32	8	25
3	3/24/32	8	30*
4	3/24/32	8	35
5	3/24/32	8	40

11.1.2. Unique neighborhood

In this variant of neighborhood, all points was involved in krige estimation. This variant is useful because of the smallest number of points (n = 118).

11.2. Neighborhood test, barium ***(Ba)***

11.2.1. Moving neighborhood

The same variant of neighborhood test was used here with follows parameters - Table 11.2.

Table 11.2. Parameters of neighborhood test for ***Ba****, the best size of the neighborhood was marked with asterisk - **

No	Min/Opt./Max	Number of Angular Sectors	XandY radius, (m)
1	3/24/32	8	20
2	3/24/32	8	25
3	3/24/32	8	30*
4	3/24/32	8	35
5	3/24/32	8	40

11.2.2. Unique neighborhood

This type of neighborhood was used in the same way as for cadmium.

12. Cross validation

Between different methods for estimation of quality of variogram fitted model the cross-validation method is one the more often using ***(Davis, M. W. 1987)***.

The quality of estimation of the "best" variogram model fitted to an experimental variogram is realized by Cross-Validation, **Armstrong, (1994, p. 143)**. The next characteristics are more important:

a/ the mean of the estimation errors to be zero

❖ *Mean Error*

$$\frac{1}{N}\sum_{i=1}^{i=n}(Z-Z^{*})=0$$

b/ the mean of standardized estimation errors to be zero;

❖ *Mean standardized error*

$$\frac{1}{N}\sum_{i=1}^{i=n}\frac{(Z-Z^{*})}{\sigma}=0$$

c/ the variance of the error

❖ *Variance of error*

$$\frac{1}{N}\sum_{i=1}^{i=n}\left(Z-Z^{*}\right)^{2}$$

d/ the variance of the standardized estimation errors to be 1.0, i. e. the slope of the linear regression of Z vs. Z* , could be close to 1.0.

- *Variance of standardized error* $\frac{1}{N}\sum_{i=1}^{i=n}\frac{(Z-Z^{*})}{\sigma^{2}}\rightarrow 1$

Two statistical parameters was using for estimation of quality of variogram fitted models - the mean of estimation errors to be zero, and the variance of the standardized estimation errors. This two parameters (***Ba***), for ordinary and universal kriging estimations, all sampling protocols and for different sampling protocols are presented in Table 12.1. and Table 12.2. consequently and in Fig. 12.1.

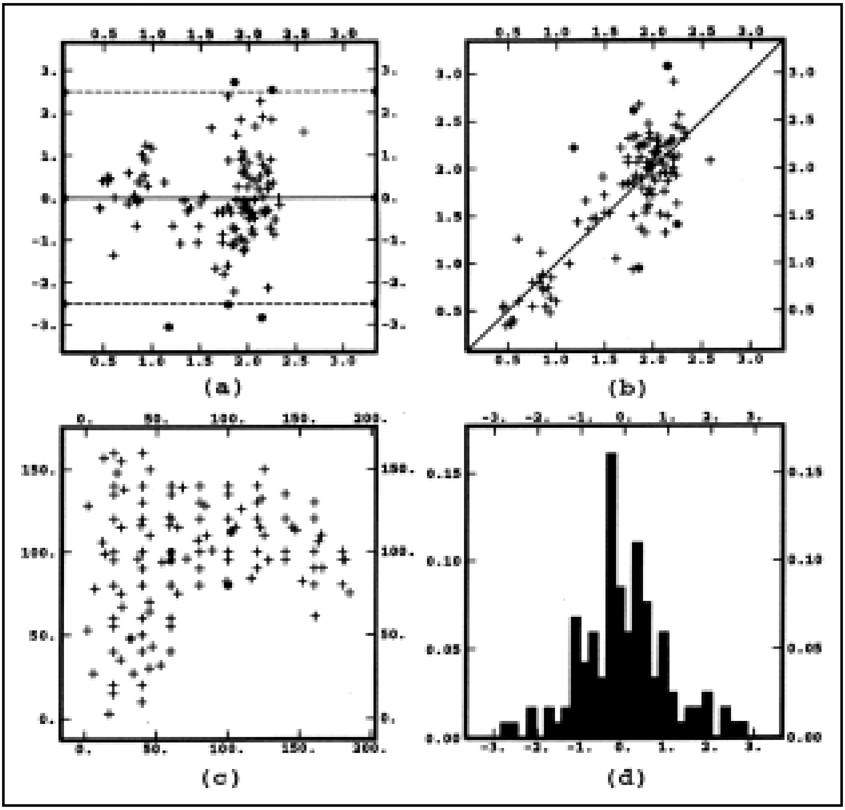

Fig. 12.1. Cross validation for ***Ba***: scatter diagrams **(a)** - (Z-Z*)/S* vs. Z*, and **(b)** - Z vs. Z*; **(c)** - base map unrobust points and **(d)** - histogram of standard errors

Table 12.1. Values of Statistics, ***Mean of Estimation Errors*** *and* ***Variance of Standardized Estimation Errors - Ba****, from Ordinary (1 and 2), and Universal Kriging Estimation (3, 4, 5), all Design Sampling Protocols - 118 points, (the best models were marked with asterisk - *)*

##	Variogram Model	**Statistics based on 118 test data**		**Statistics based on robust data**		Number of robust points
		Mean of the estimation error, µg/g	Variance of the stan-dardized estimation errors	Mean of the estimation error, µg/g	Variance of the stan-dardized estimation errors	
1	**OMNI** Moving Neighb., all protocols	-7.8	1.082	1.0	0.797	113
2	**OMNI*** Unique Neighb., all protocols	-4.4	1.106	-2.2	0.882	114
3	**0°** Isotr.+ Drift Moving Neighb., all protocols	-6.9	1.348	-4.9	0.845	110
4	**0°*** Isotr.+Drift Unique Neighb., all protocols	-6.2	1.332	-4.2	0.839	110
5	**45°*** Isotr.+Drift Moving Neighb., all protocols	13.1	0.997	12.6	0.884	116
6	**45°** Isotr.+Drift Unique Neighb., all protocols	-2.5	0.945	15.6	0.843	116

Table 12.2. Values of Statistics, ***Mean of Estimation Errors*** *and* ***Variance of Standardized Estimation Errors - Ba****, from Ordinary (1 and 2), and Universal Kriging Estimation (3, 4, 5), all Design Sampling Protocols - 118 points, (the best models were marked with asterisk - *)*

##	Variogram Model	**Statistics based on 118 test data**		**Statistics based on robust data**		Number of robust points
		Mean of the estimation error, µg/g	Variance of the standardized estimation errors	Mean of the estimation error, µg/g	Variance of the standardized estimation errors	
1	**OMNI** Unique Neighb., R protocol	14.8	1.039	14.8	1.034	40
2	**45°*** Isotr.+Drift Unique Neighb., R protocol	-3.0	1.008	-0.3	1.008	40
3	**OMNI** Unique Neighb., H protocol	17.2	0.834	17.2	0.834	39
4	**45°*** Isotr.+Drift Unique Neighb., H protocol	-9.5	1.007	-9.4	1.007	39
5	**OMNI** Unique Neighb., S protocol	2.8	0.967	2.8	0.967	39
6	**45°*** Isotr.+Drift Unique Neighb., S protocol	-14.8	1.008	-14.8	1.008	39

13. Kriging estimation

13.1. Ordinary Kriging (model omnidirectional variogram) - Cadmium ***(Cd)*** and Barium ***(Ba)***

To estimate the values of the blocks in a regular grid we use the Ordinary Kriging method. The dimensions of the 2D blocks are 20 m by 20 m. We may obtain the best Ordinary Kriging estimation of the blocks through adjusting of variogram model and choosing the neighborhood, moving (angular sectors) for barium Fig. 13. 1. (isolines) and cadmium (***Cd***<13 μg/g) Fig. 13.2.

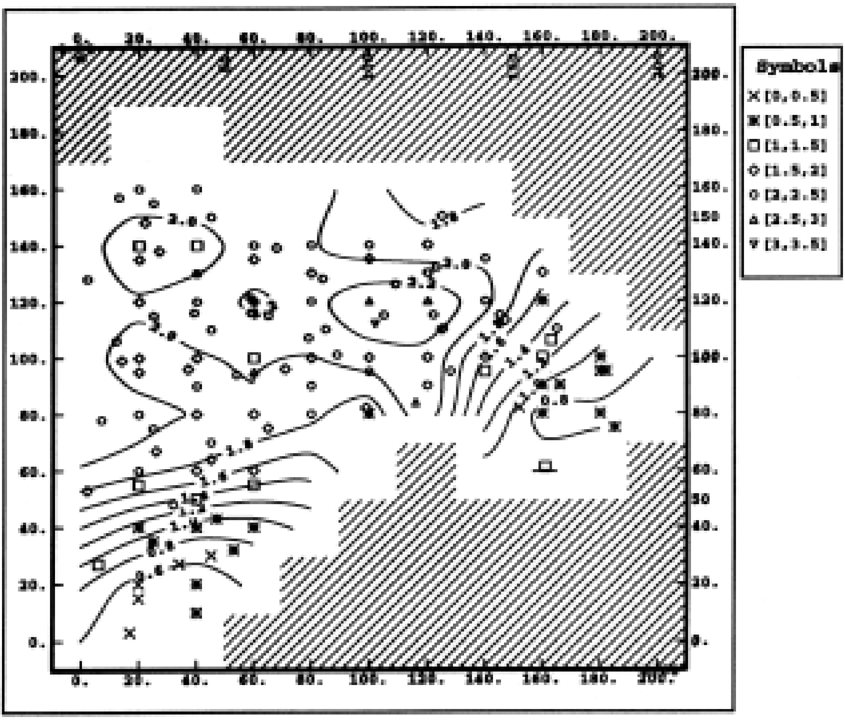

Fig. 13.1. Ordinary Kriging block estimation for barium, all protocols - isolines

The standard deviation of Ordinary kriging estimation for cadmium was shown in Fig. 13. 3. (isolines).

13.2. Universal Kriging (model underlying variogram)

13.2.1 Some theoretical aspects

In the terms of geostatistics if the regionalized variable Z(x) is not stationary it may be decomposed into two components

(13.1.) $$Z(x) = Y(x) + m(x)$$

where: Y(x) - underlying variogram, isotropic
m(x) - the drift, which may be defined as either first order,

(13.2.) $$m(x) = a_0 + a_1 x_1 + a_2 x_2$$

second order

(13.3.) $$m(x) = a_0 + a_1 x_1 + a_2 x_2 + a_3 x_1^2 + a_4 x_1 x_2 + a_5 x_5^2$$

or higher, where x_1 and x_2 are the geographic coordinates of the point within the neighborhood, and ***a'***s are unknown drift coefficients that must be found.

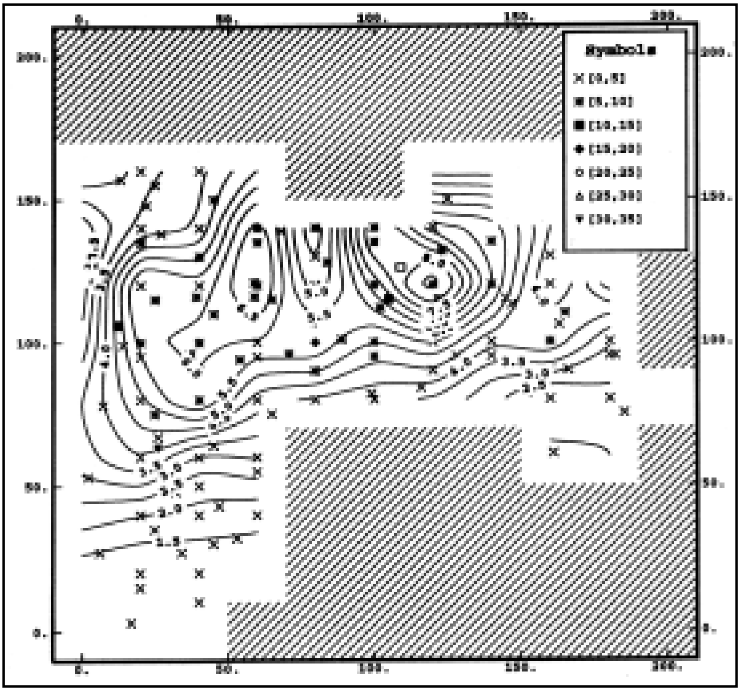

Fig. 13.2. Ordinary Kriging block estimation for cadmium, all protocols - isolines

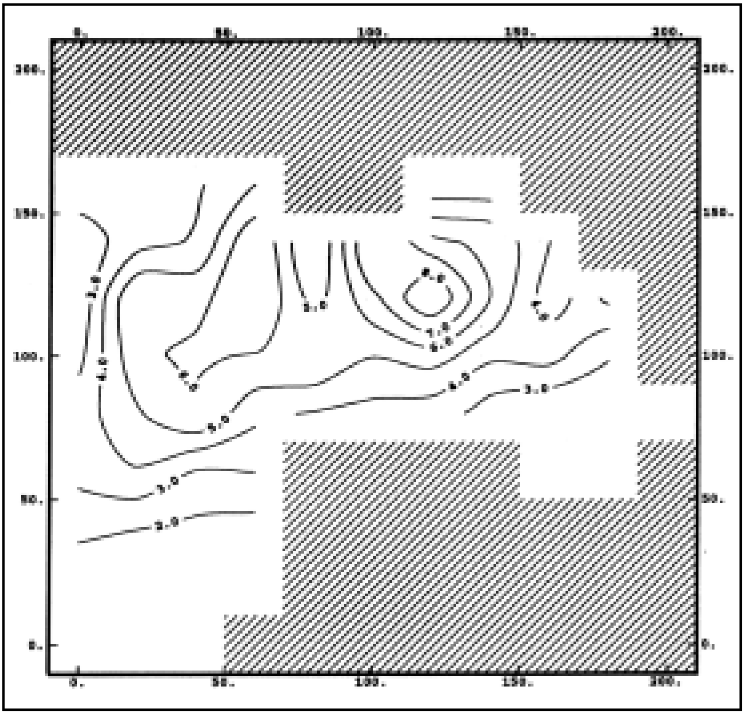

Fig. 13.3. Standard error, Ordinary Kriging block estimation for cadmium, all protocols - isolines

13.2.2 Universal Kriging using for estimation of barium ***(Ba)***

This technic was used for estimation of barium because of two reasons:

a/ the drift are presented in the space distribution of barium. Statistically significant coefficient of correlation (r=0.6143) between concentration of barium and Y co-ordinate, desribed by equations (13.4.) and (13.5.) was shown on Fig. 13.4.,

(13.4.) $X = 0.010856 \times Y + 0.663771,$

(13.5.) $Y = 34.73431 \times X + 36.777849.$

b/ unbounded (nonstationary) behavior of experimental variograms for barium ***(Ba)***, all sampling protocols, Fig. 10.10 and Fig. 10.11.

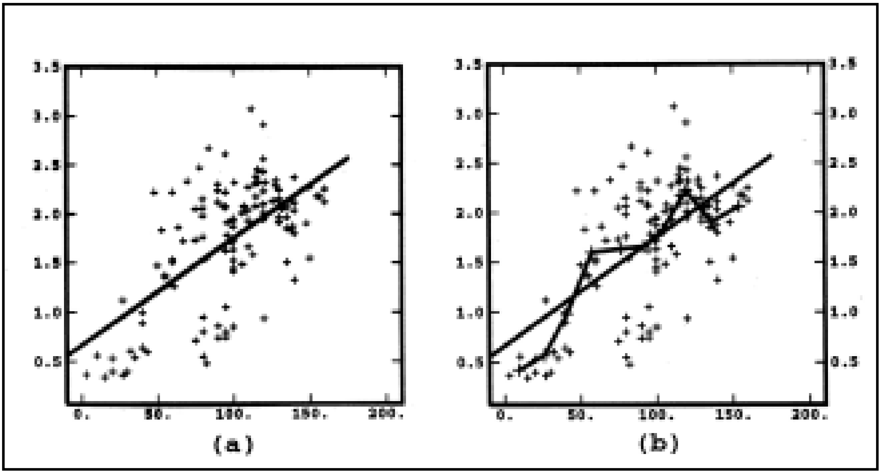

Fig. 13.4. Space correlation between: (a) concentration of barium and Y co-ordinate for all sampling protocols and (b) their conditional expectation. The coefficient of correlation (r = 0.6143)

IV Interpretation of the results

14. Comparison between different sampling protocols

Comparison between different design sampling protocols for barium was performed through two ways (details about them are explained in the next paragraph). However for cadmium was used just some simple proportions, (Ramsey et al., 1995).

14.1. About the methods using for determination of the best sampling design protocol

Two ways for estimation was used. The first one comes from krige estimation of cadmium and barium, however the second one was based on same simple proportion between the mean in the protocol and the grand mean, Ramsey et al. (1995).

14.2. Differentiation of the bias sampling protocol through krige estimation

14.2.1. Comparing between Herringbone and Stratified samples protocol versus Regular sampling protocol

Comparing versus regular protocol lead that it is a best sampling design protocol. Graphically this conclusions was shown on Fig 14.1.

14.2.2. Comparing between Regular and Stratified samples protocols versus Herringbone sampling protocol

The results is very similar to the previous one except the worse parameters, (Fig. 14. 2.).

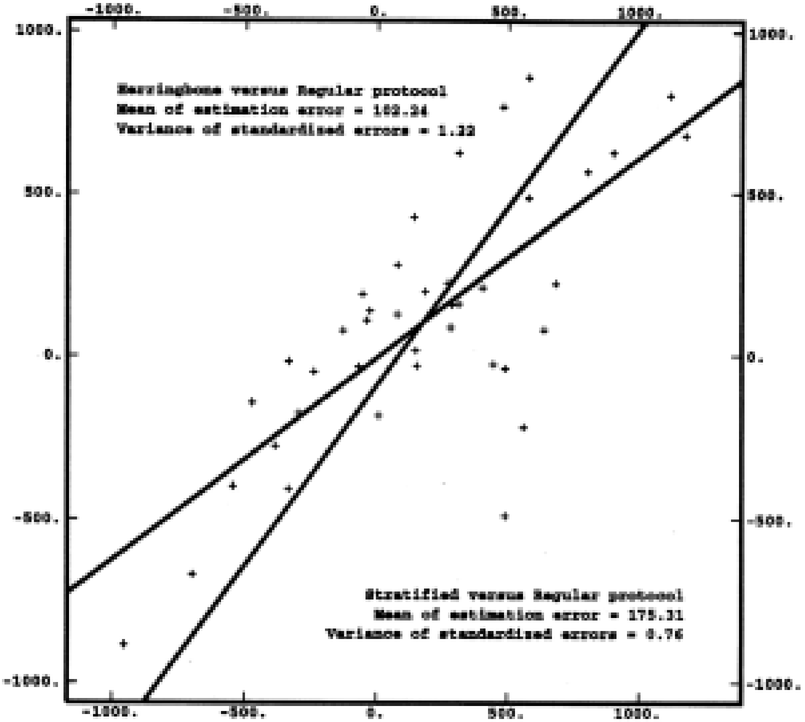

Fig.14.1. Correlation Zs*-Zr/Zh*-Zr Estim.

14.2.3. Comparing between Regular and Herringbone samples protocols versus Stratified sampling protocol

This sampling protocol is with lowest dispersion, however the estimation is shifted to the size of overestimation. Fig. 14. 3.

14.3. Estimation of bias sampling protocol by simple proportion between the means and an grand mean

Results obtained by using of this methods was presented in Table 14.1. The best sampling protocol for cadmium is the regular one and for barium the herringbone one.

14.4. Geostatistical point of view on the efficiency between different design sampling protocols

Some geostatistical approaches concerning different sampling design protocol are explained in (Delfiner, P. et al. 1987). The efficiency between three different sampling design protocols (Regular, Herringbone and Stratified Random) was performed through the concept of variance of extension and its relationship to the variance of

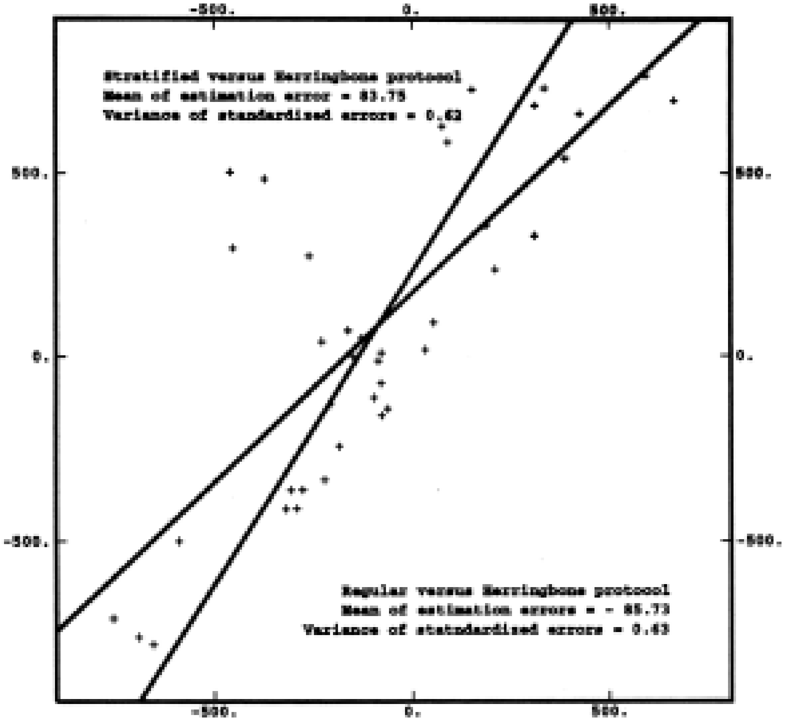

Fig.14.2. Correlation Zr*-Zh/Zs*-Zh Estim.

*Table 14.1. Bias Statistics (**Cd** and **Ba**) for Regular, Herringbone and Stratified Random Design Sampling Protocols, after: **Ramsey et al. (1995)***
*(the best sampling protocols were marked with asterisk - *)*

##		**Regular protocol**	**Herring bone protocol**	**Stratified random protocol**	**Grand mean, all protocols**
1	## of samples	40	39	39	118
2	Mean value ***Cd***, µg/g	4.626	5.494	4.332	4.816
3	Bias ***Cd***, % from Grand mean	-3.945*	14.078	-10.049	- -
4	Mean value ***Ba***, µg/g	1642.47	1711.79	1771.21	1707.93
5	Bias ***Ba***, % from Grand mean	-3.832	0.226*	3.705	- -

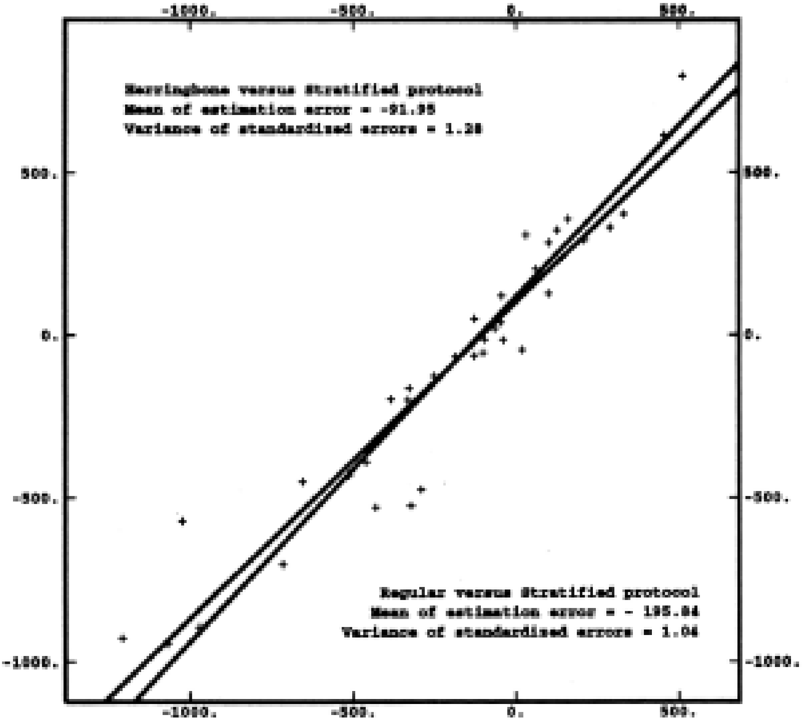

Fig.14.3. Correlation Zr*-Zs/Zh*-Zs Estim.

dispersion (Delfiner, P. et al. 1987, p. 78). Efficiency of the regular sampling design protocol is more than the efficiency of the stratified random design protocol, however if the size of the grid box of the sampling protocol “becomes to be large with respect to the range of the variogram”, (62 m) “this advantage fades away...”

Conclusions

The data was presented in the studied area by 118 samples in three different sampling protocols (40 points for regular and 39 points for herringbone and stratified random).

Geochemical behavior of concentrations of cadmium ***(Cd)*** and barium ***(Ba)*** was formalized in terms of geostatistics as regionalized variables in inclined in 6° alongY axis (to SW direction), tabular, homogenous soil body, with quite irregular shape in 2-D space. The nature of geochemical variability of cadmium (***Cd***) and barium ***(Ba)*** was mixed and they are product by natural variability and variability caused of human activity.

The concentrations of cadmium (***Cd***) varied in wide interval (0.5-32.0 µg/g) in two mixed lognormal distributions:
a/ 0.5-1.5 µg/g, caused by natural variability;
b/ 1.9-32.0 µg/g (with probability, p=0.80), was caused by human activity (lead smelting artisan in 1300 - 1550 AD.

Variability of cadmium (***Cd***) in studied area is high (coefficient of variation = 0.79).

Barium's (***Ba***) concentration are between 345 and 3070 µg/g, in one normal distribution and with low variability (coefficient of variation = 0.37).

Estimation of the values for cadmium (***Cd***) (in blocks 20 m by 20 m) performed with Ordinary Kriging procedure give us satisfactory results. High concentration are located in the central part of the studied area into two local places, which containes all outliers, (***Cd*** < 13 µg/g).

Estimation of the values for barium (***Ba***) (in blocks 20 m by 20 m) performed with Ordinary and Universal Kriging procedure give us two very similar estimations of concentrations. The second one is more omtimistic (extended outside of studied area).

The best sampling design protocol for barium (***Ba***) is a regular one.

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