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Cumulative Semivariogram Models of Trace Elements from Springs in Saudi Arabia

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Trace elements are rarely distributed in earth's crust and they are invariably in low concentrations. Due to this low concentration they are not analyzed by conventional hydrochemical methods but by rather special techniques with great care. The trace elements are especially useful in detecting the origin of the groundwater in an area. Their regional distribution helps to obtain significant clues on the groundwater movement and mixture processes. It is proposed, herein to assess the trace element concentration available at far distant points by employing the cumulative semivariogram models. These models furnish further systematic interpretations about trace element areal extends, concentration directions, groundwater movement and its continuity.

Introduction

A water spring is a place where without the agency of a man made structure, water flows from a rock or soil over the land or into a body of surface water. It has various characteristics such as the character of opening through which water issues, force that brings the water to the surface, lithologic character of the original aquifer of water source; quantity as well as quality of discharged water, uniformity in discharge rates, temperatures, and features produced by springs.

In arid and semi-arid areas, the water in the past was obtained by natives from different sources; namely springs, streams, rivers, lakes and groundwater.

Saudi Arabia is one of the arid regions which extends over an areas of about 2.25 $\times 10^6$ km^2. Springs represent the location of an ancient settlement and many of the

Saudi Arabian major towns and villages have depended until recently on spring waters for a good proportion of their potable agricultural and irrigation demands.

Number of papers were published on the springs of Saudi Arabia such as by Roy (1961), Dincer (1974), Berthier *et al.* (1981), Al-Khatib and Khan (1982), Tayeb and Taha (1984), Abderrahman and Ukayli (1984), Al-Naeem (1987), Bazuhair and Hussein (1989), Bazuhair, *et al.* (1990) and Hussein *et al.* (1990).

The above mentioned authors studied the spring waters in different topics such as their classification, qualitative and quantitative studies either for a certain number of springs within a region or at certain locations within Saudi Arabia.

Trace elements although low in their concentrations provide additional supplements in groundwater quality assessment studies. Their classical treatment is already available in standard textbooks such as Matthes (1980). These studies reveal information concerning the mineral deposit location, origin of the groundwater and assessment of their use for domestic and irrigation purposes.

The statistical treatment of trace element data is exposed by Eriksson (1985) by conventional methods. However, all of the studies available on trace elements either qualitatively classify them into certain groups or standard variation for different purposes or present summary statistics for the overall average behaviors of trace elements.

However, this paper has its originality both in collection of trace element data for the first time in the Kingdom of Saudi Arabia and the application of cumulative semivariogram (CSV) technique in their regionalization. The CSV method as proposed by Şen (1989, 1991) provides answers to basic questions such as the areal extent of trace elements their extreme concentrations within a regional continuity, mixture, *etc.*

It is the main purpose of this paper to present the CSV application to the trace elements data and derive interpretations, conclusions and predictions thereof. The regional model for individual trace elements are derived from the experimental CSV and the regional correlation coefficients are obtained. These values assist dynamic interpretations for the trace elements with their heterogeneous geological environments. The methodology presented herein can be applied to similar problems in any other part of the world.

Cumulative Semivariogram

It is a technique whereby the degree of regional variabilities is qualified with a simple algorithm. Various other methodologies such as ordinary variogram (Matheron 1963) and variation techniques have been proposed for regionalizing point-spatial data. There were some drawbacks in their applications (Şen 1989). Classical autocorrelation methods cannot be applied to trace element data because a prerequisite is that the data must have normal distribution. However, so far worldwide experience have indicated that trace element data are never normally distributed. The relevant distributions for those elements are mostly in negative exponential or rarely log-normal forms. Neither of these distributions are suitable for variance or correlation studies. On the other hand, the semivariogram model although, gets rid of these drawbacks it yields reliable results only when the locations are regularly distributed in a given region. It has to be mentioned at this stage that the classical semivariogram, autocorrelation and autorun (Şen 1977) techniques all require equally spaced data locations. However, the groundwater sample locations which coincide with well and or spring locations are all irregularly distributed in a region. Consequently, all of the classical methods is highly questionable in these situations except that they provide approximate results only.

However, the CSV method gives always reliable results in the form of a non decreasing change with ordered distance based on any data location pattern whether regular or irregular.

One can write in general the CSV expression as

$$\nu_c(h_k) = \sum_{i-1}^{k} d(h^i) = \frac{1}{2}\sum_{i-1}^{k} (z_i - z_{i-1})^2$$

where $d(h^i)$ indicates half-squared difference at i-th order in an ordered trace element distance sequence. Herein, superscript i does not mean a power, but rather the rank; z_i 's are the trace elements value in ppb at i-th rank.

Data Acquisition

This paper represents the first quantitative study for the trace elements in spring waters of Saudi Arabia. It involves study of twenty springs at different locations in Saudi Arabia (see Fig. 1).

The water samples were collected in polythene bottles, prior to sampling the bottles were soaked in 20% (v/v) nitric acid for twenty-four hours. Subsequently, they are washed several times with distilled water to remove traces of the acid, then dried and closed firmly.

However, in the field the containers were washed with the water to be sampled and then the samples were taken and the bottles were closed.

Nine elements in each spring water were traced while others were either very hard to detect or nil. The detected elements are Li, Pb, Al, Mn, Fe, Si, Ba, Ni and Sr. The analyses were carried out at the Faculty of Earth Sciences Laboratory using Perkin:-Elmer 5000 device. The whole samples were clear of colloid and therefore the filter step was not required.

The water of springs issues either from the hard crust of igneous and metamorphic rocks as well as alluvium or soft rocks such as sandstone and limestone. The

Table 1 – Trace Elements Concentration in (ppb)

Location and Statistics Param.	Li	Pb	Al	Mn	Fe	Si (×100)	Ba	Ni	Sr
Tabuk			650	93	360	257	71	1430	175
Al-Jouf			600	230	321	74	160	1600	50
Al-Ula			910	80	350	163	80	2000	170
Al-Qaseem			771	92	335	65	150	1888	124
Khaybar			1150	90	360	51	20	2000	29
Yanbu'AlNakhl	740		700	3000	1150	51	5000	2520	180
Wadi Al-Farra	–		1001	90	406	60	8	1703	–
Al-Qatif			950	85	340	28	63	1300	440
Al-Hassa			350	95	250	56	4000	1940	240
Al-Kharj	–		1028	104	351	93	49	1510	–
Al-Kamel			750	92	365	46	180	1500	42
Wadi Gudaid		1425	650	2100	250	187	2000	2500	120
Wadi Khulais	–	–	–	–	–	56	–	–	–
Wadi Fatima	–	–	–	–	–	70	–	–	–
Al-Sharyee	–	–	–	–	–	126	–	–	–
Al-Taif	750		526	99	390	168	98	1644	50
Al-Aflaj		1200	860	3000	345	28	5100	2500	560
Abha			700	94	340	47	62	1900	50
Jizan			1047	225	328	102	104	1409	468
Al-Lith	–	–	–	–	–	163	–	–	–
Sample Size	14	16	16	16	16	16	16	16	14
Average	591	767	724	598	390	93	1076	1834	193
Mode	620	697	650	90	340	51	98	2000	50
Stand. Devi.	188	261	251	1061	207	61	1873	399	175
Range	720	1094	932	2920	900	23	5080	1220	531

first group is called the Arabian Shield and the other one the Arabian Shelf. Details of the geological classification are given already by Bazuhair and Hussein (1989).

In areas like Saudi Arabia, collection of water samples from twenty locations is costly as well as hard work. The results of the analyses are shown in Table 1.

The tabulated values of concentrations are the average of three runs of analysis for each sample. The dicussion about the origin of these trace elements is rather wide and a number of text books are available in any library. Although the standard unit in expressing trace element concentrations is microgram/liter, it is a common practices among hydrogeologists to use its equivalent form as (ppb), *i.e.*, parts per billion. Throughout this paper ppb is employed due to its practical convenience.

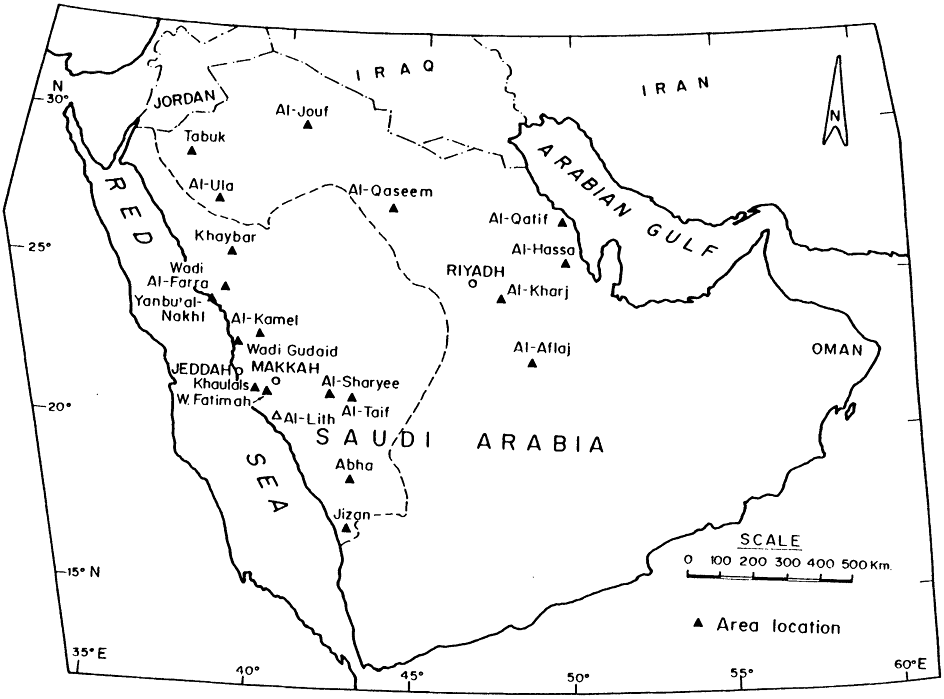

Fig. 1. Location Map.

The major sources of the trace elements are the hard rocks in the Arabian Shield. The results show that some elements have high concentration in the soft rocks within the Arabian Shelf far from the source location. This reflects and confirms the recharge from west area toward east direction controlled by geographical features. Table 1 shows some statistical parameters which explain the general concentration facts in Saudi Arabian trace elements.

Cumulative Semivariogram Application

The classical cumulative semivariograms are robust and valid whatever the underlying distribution function is. The validity is mainly due to the central limit theorem in statistical literature which states that whatever the underlying probability distribution of a variable, such as trace elements, its successive summations are averages and will have approximately normal distribution. The experimental CSV's for each trace element are presented in Figs. 2-10. It is to be noticed in all of these figures that the horizontal axis is given up to 10 km whereas it is evident from Fig. 1 that maximum distance is about 1,300 km. After 10 km the CSV values fluctuate around the straight line extension. Prior to any quantitative analysis if possible to depict the following significant points:

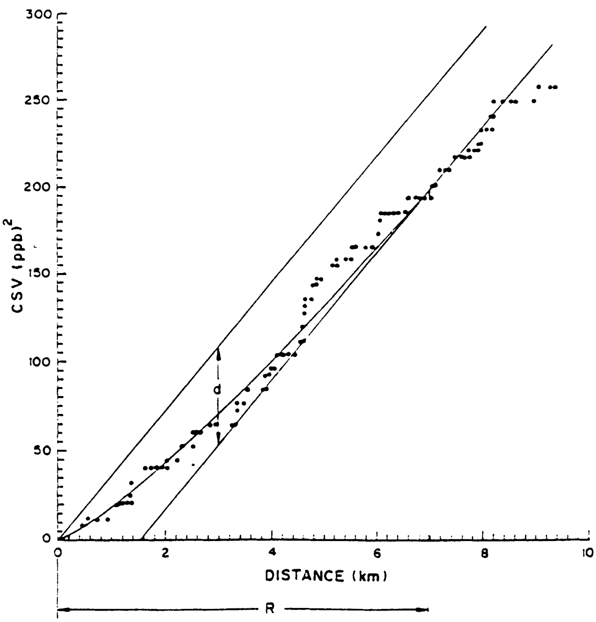

Fig. 2. Experimental standard CSV for Mn.

i) All of the CSV's in Figs. 2-10 have almost continuous change with distance without significant discontinuities in terms of sudden changes. In addition, none of them has periodic changes. These indicate that the evolution of trace elements within the study area are not subject to major regional changes. Besides, the geological environment for their evaluation is almost uniform.

ii) Some of the CSV's appear as straight lines such as in Figs. 3, 4, 9, and 10. This implies that the trace element (Fe, Si, Al and Li) occurrences, within the region considered have a random behavior. In other words, these trace elements arise from an independently evolving process. There appears no effect of trace element occurrence of one site from the trace element occurrences at other locations. Furthermore, geological elements giving rise to these trace elements are rather uniformly scattered within the study area.

iii) It is also interesting to notice that among four straight line CSV's only the one in Fig. 3 crosses from the origin whereas, others have a non-zero intercept on the distance axis. Crossing of the CSV from the origin implies a perfect randomness for the original behavior of the trace element which is Fe in this case. This is tantamount to saying that Fe concentration at any site cannot be estimated from the information available at any other site.

On the other hand, CSV's in Figs. 4, 9, and 10 all have positive intercepts on the distance axis. Such an intercept implies that along a certain distance which is equal to the intercept value, the underlying trace element has zero CSV. Subsequently, zero CSV value indicates perfect correlation of trace elements which are apart from each other less than or equal to this distance.

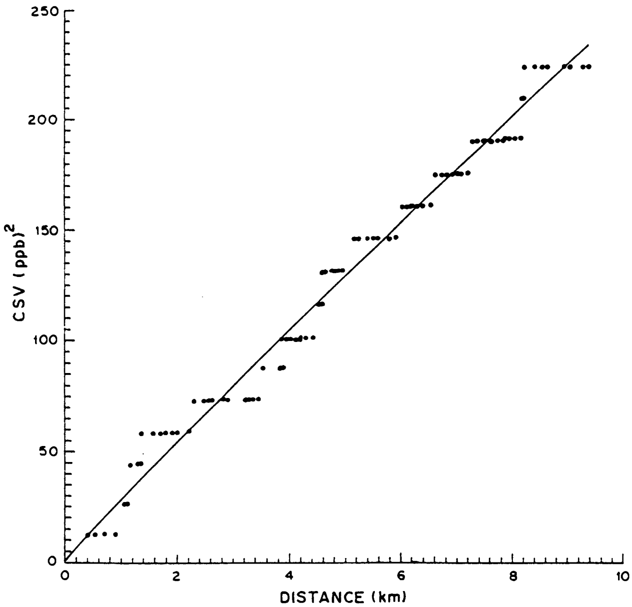

Fig. 3. Experimental standard CSV for Fe.

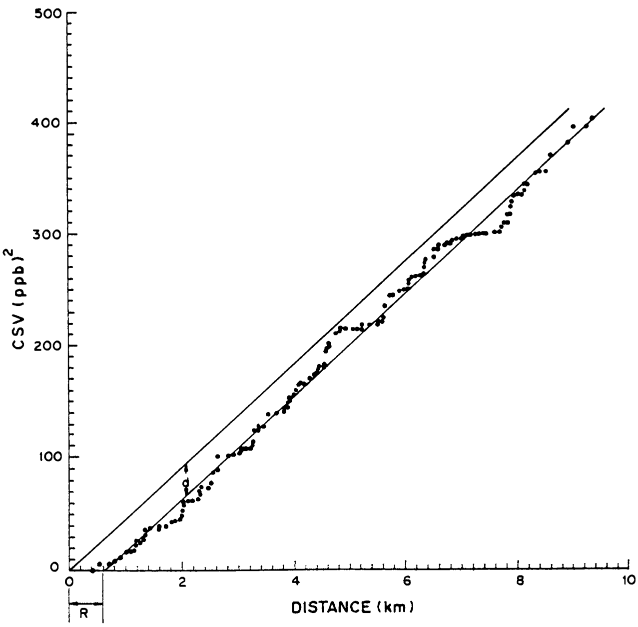

Fig. 4. Experimental standard CSV for Si.

For instance, Si concentration CSV in Fig. 4 indicates almost 0.6 km intercept. Hence, around any site within the area of a circle 0.6 km in radius the Si trace element concentration can be regarded as equal to each other. As a result of this, Si does not change significantly within short distances. Similar interpretations can be deduced for Al and Li.

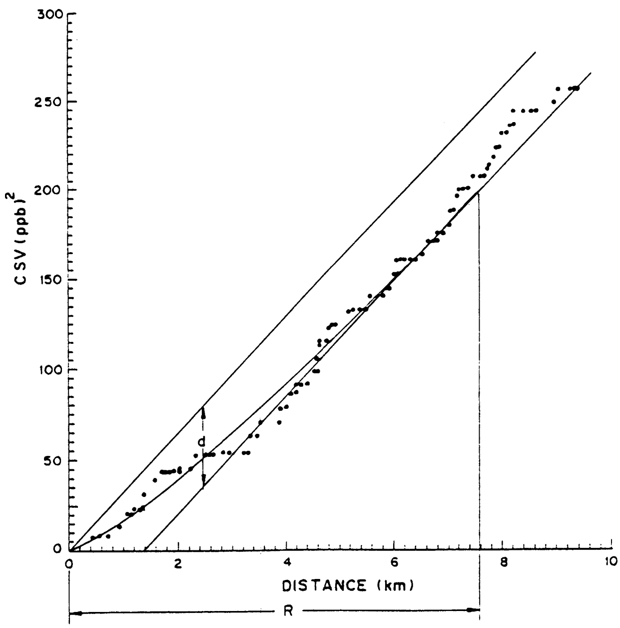

Fig. 5. Experimental standard CSV for Ba.

iv) The remaining CVS's in Figs. 2, 5-8, does not appear as a straight line passing through the origin. This is equivalent to saying that these trace elements within the area cannot be considered as independent processes, but they all emerge from dependent processes. This further indicates that in the evolution of trace elements (Mn, Sr, Ba, Pb and Li), uniform geological conditions did not prevail but rather a complex combination of sources took place concurrently and sequentially.

v) That the initial portions of each experimental CSV in Figs. 2, 5-8, 6-9 shift toward the distance axis. Such a shift implies the existence of positive regional correlation within the trace element regional variation. It further implies that large trace element values follow large values and small values follow small values.

vi) It is obvious from Figs. 2, 5-8, 6-9 that each experimental CSV fluctuates about a straight line at large distance. This is an expected result of central limit theorem. With the start of such late straight line the trace element values become completely independent of each other. Local deviations from the straight line indicates the hidden or minor dependencies in the trace element evolution. However, this point falls outside the scope of this paper.

vii) Over the initial distance, R, the experimental CSV's of Figs. 2, 5-8, 6-9 appear as a curve. This distance is referred to as the range of influence and defined quantitatively as the distance between the original point and the abscissa of the initial point of the late straight line portion as mentioned in the previous step.

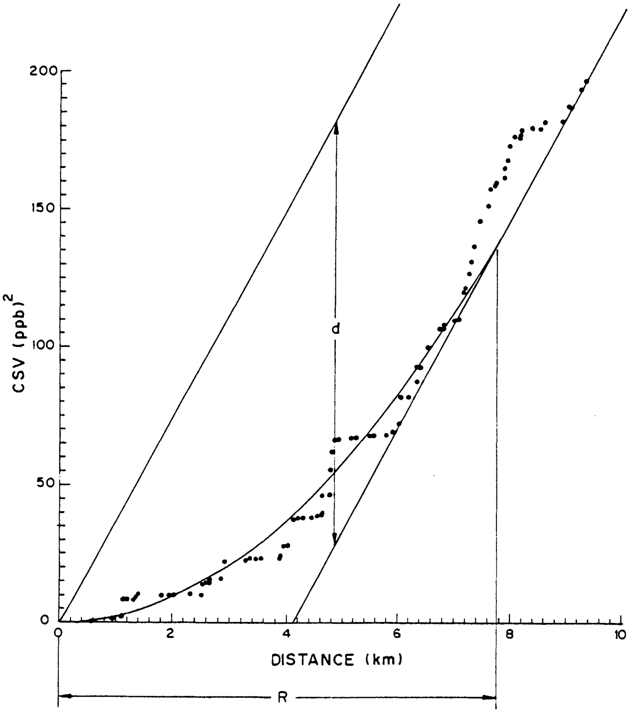

Fig. 6. Experimental standard CSV for Sr.

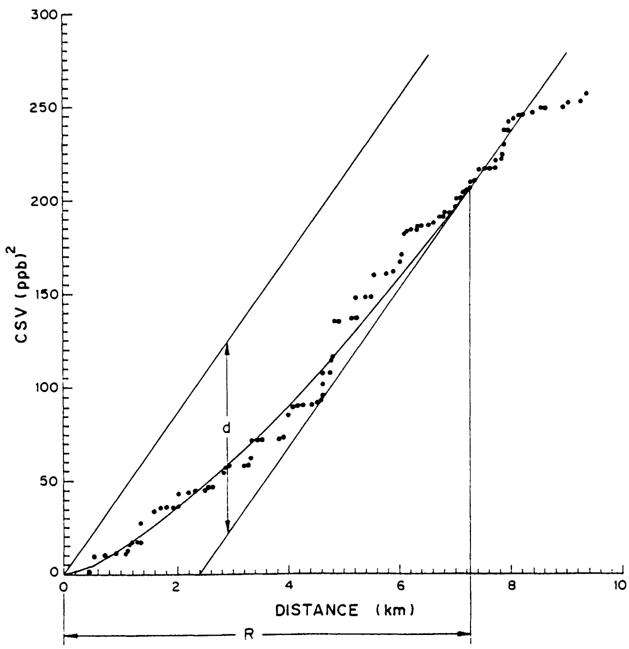

Fig. 7. Experimental standard CSV for Pb.

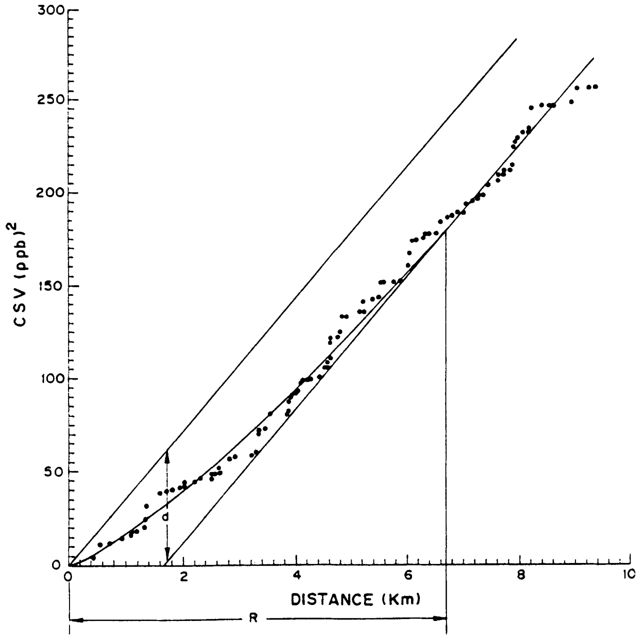

Fig. 8. Experimental standard CSV for Ni.

viii) The slope of straight lines in Figs. 3, 4, 9, 10 and/or late distance straight line slopes in Figs. 2, 5-8 are related to the standard deviation of the underlying trace elements regional variation. The steeper the straight line the greater will be the standard deviation. It is possible to consider this slope as the population standard deviation of the trace elements.

ix) The vertical distance between the late distance straight line and the one drawn parallel to it passing through the origin reflects the magnitude of regional correlation coefficient of the trace element. Obviously, the smaller the distance, the smaller will be the trace element regional correlation (Şen 1991).

x) It is possible to deduce type of trace element regional evolution model from the shapes of experimental CSV. For instance, the existence of late distance straight line implies that the underlying generating mechanism of trace elements is Markov process. On the other hand, complete straight lines as in Figs. 4, 9 and 10 with intercepts proves that the regional generating mechanism is of moving average process type. However, zero intercept straight line implies an independent process Şen (1991).

xi) Curve fitting technique to the experimental CSV with least squares method leads to suitable models for individual CSV. Such models constitute the basis of Kriging technique through which is is possible to obtain the regional map for each trace element. For the sake of brevity the use of Kriging technique is left outside the scope of this paper.

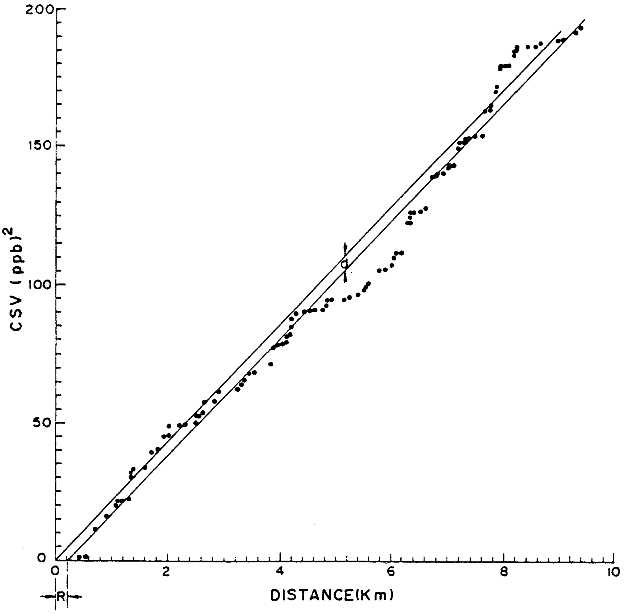

Fig. 9. Experimental standard CSV for Al.

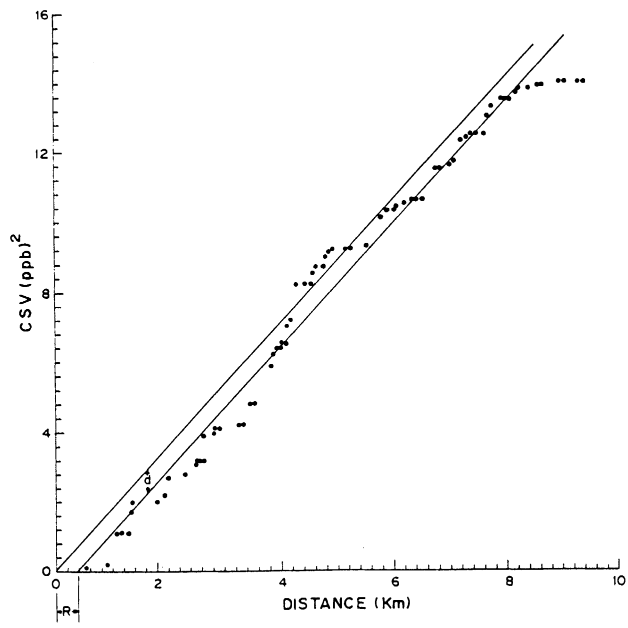

Fig. 10. Experimental standard CSV for Li.

In the light of the above mentioned points the relevant numerical values concerning the intercepts, radius of influences, vertical distances, standard deviations and types of CSV models are summarized in Table 2.

Table 2 – Cumulative Semivariogram Characteristics

Parameter	Mn	Fe	Si	Ba	Sr	Pb	Ni	Al	Li
Intercept (km)	–	0	0.6	–	–	–	–	0.2	0.4
Range of Influe. (km)	7	–	–	7.6	7.8	7.29	6.6	–	–
Stand. Deviation (ppb)	1061	207	6100.0	1873.0	2.0	261.00	399.0	251.0	188.0
Vertical Distan. $(ppm)^2$	50	0	26.0	43.0	150.0	100.00	60.0	26.0	0.6
Type of Model	Power	Linear	Linear	Power	Power	Power	Power	Linear	Linear

Conclusions

One of the significant questions about the trace elements is whether they have independent or dependent occurrences within a given region. In the past, trace elements were assumed to evolve independently in a region. Consequently, their interpretations lead to limited amount of information which was obtained by classical statistical techniques only. The main difficulty was missing of an objective technique to measure regional correlation. However, in this paper cumulative semivariogram (CSV) technique is proposed as a practical tool in regional studies.

The CSV calculations are easy and have no ambiguity. The CSV's show the change of half squared differences between intact lengths with ordered distances. The shapes of experimental CSV's yield useful information as to the regional correlation coefficient, ranges of influence, types of evolution models, hidden or local variations.

It is hoped that in future studies such approaches will be applied to trace element regional modeling by Kriging technique.

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