Forecast Estimation of Heavy Metals Values in a Soils

T. Koroleva

Institute of Ecology of TAS, Russia
E-mail: Tata.Koroleva@ksu.ru

Abstract: Recently problem of accumulation of heavy metals in an atmosphere, soils both waters in the natural and antropogently-modified landscapes is characteristic for many countries of the world. The soil can be considered as the integrated indicator of long-term process of pollution of an environment giving representation about quality of environments connected with soil - air and waters. The influence of heavy metals on an environment constantly amplifies in process of increase of scales and intensity of economic activity of the people, and the knowledge of laws of spatial distribution of heavy metals becomes urgent necessity.

The various analytical methods are applied to research of the spatial concentration of heavy metals in soils. At the same time it is necessary to carry out a polyelement estimation of soil and to take into account variety of the factors at absence of the information a priory on probable distribution of heavy metals in a soils, which, is rather complex systems. Such necessity dictated development of a method of a grouping soil given for a forecast estimation of the concentration of heavy metals in soils on a basis of the cluster analysis. As model object were used of soils of Predvolgie of Tatarstan Republic.

The forecast estimation of the concentration of heavy metals in soils is carried out by application of a method of a grouping of soil date by concentration of heavy metals, on the basis of linguistic clusterisation, consecutive estimation procedure and fuzzy sets.

With the purpose of reception of estimated concentration of heavy metals in soils of Predvolgie the data on the basic physical and chemical parameters of soils, concentration of six heavy metals were used: lead, copper, nickel, zinc, chromium, manganese, and also rank estimations of an ecological condition of territory and total emissions of polluting substances in an atmosphere on a card of an ecological situation of Tatarstan Republic. The sharing of quantitative and qualitative parameters is characteristic for the analysis of a condition of soils for the complex approach to an estimation of territory.

Keywords: heavy metals, forecasting, linguistic clusterisation

1 Method of data soil grouping for estimation of the concentration of heavy metals

Forecast of heavy metals concentrations in soil made by updating a method global clusterisation on the basis of linguistic clusterisation. The main physical and chemical data soil, concentration of six heavy metals (Pb, Cu, Ni, Zn, Cr, Mn), the balls estimations of an ecological condition of territory and total emissions HM in an atmosphere on a card of an ecological situation of Republic Tatarstan, were used with the purpose of forecast concentration of heavy metals in soils of Predvolgie of Tatarstan Republic.

The method of an estimation of the concentration of heavy metals in soil is given below on an example of a grouping of the soil data on nickel total form.

The task is reduced to allocation in multivariable space subspace of attributes of natural congestions of objects, which are homogeneous in sense variability by groups and are described by normal distribution. During mathematical data processing the problem of reduction of dimension of a task is solved, i.e. those attributes are allocated only which rather well characterise behaviour of heavy metals. The similarity between structures is determined by three elements: the form, dispersion (variance), shift. Among them the variance describing mutual behaviour of researched parameters, instead of their functional dependence and absolute meanings is used in developed method.

The analysed matrix of the soil data has dimension 6×96. Below physical and chemical parameters of soil are given:

(1) Sum of emissions
(2) Ecological conditions
(3) Humus
(4) Sum of the bases
(5) Silt
(6) Nickel total form.

The grouping of the data on parameters is carried out complete sort out of all possible combinations of parameters. For them are consider as equal in rights following combinations:

(123456)
(1)(23456)
...
(1)(2)(34) (56)
…
(1) (2) (3) (4) (5) (6)

The method is constructed as consecutive recurrence subprocedures for each of combinations of parameters:

① Finding of preliminary splitting by consecutive procedure. Two values (n_0) for one parameter are separated, are calculated average and variance of sample. The size cluster is determined under the formula:

$$N = \left[\frac{t_{n_0}{}^2 S_{n_0}^2}{\delta^2} \right] + 1$$

The right part of the formula is guarantee moment of a stop, where t_{n_0} : quantile of Student distribution, $S_{n_0}^2$: variance of sample, δ: half-width-confidence-interval having for the user sense of a general mistake of measurement.

N values are separated, average and variance of sample are recalculated. For *N* it is more or equal guarantee moment of a stop the initial splitting is achieved. If the group contains more than one parameter, the size cluster will be equal to a maximum from the sizes clusters on all parameters which are included in the group (Fig.1):

$$N = \max (N1, N2, N3, N4, N5, N6)$$

The final size of cluster is determined by specification of final splitting.

② Specification of final splitting. At viewing the next splitting of a matrix the line is transferred from one group of parameters in another, and the change functional is counted up which gives such moving:

$$I = \frac{1}{N} \sum_{s=1}^{k_1} \sum_{t=1}^{k_2} \sum_{\substack{j \in G_s \\ I \in \Re_{ts}}} (x_{ij} - \bar{x}_{ts}^{j})^2$$

Where $\bar{x}_{ts}^{j}$:average *j* components of lines making *t* a class on *s* to group of parameters; k_1: number of groups; k_2: number of classes; $\Re_{ts}$: subset of indexes of objects *t* of a class in *s* to group of parameters.

Minimal value of calculated functional indicate, that the combination have optimum splitting. So, this value is equal 0.7098 and combination of parameters is next: (1), (2), (34), (56) (Fig.1). The optimum splitting of parameters includes 13 clusters.

③ Analysis of clusters.

The map of 13 clusters is given on Fig.2. From a map clusters it is visible, that as a result of an optimum grouping Ni (total form) and the Silt are in one cluster, i.e. there is connection between the total form of Ni and oozy fraction. For these parameters there are 3 clusters (4.1, 4.2, 4.3), each of which is described average and variance.

	1	2	3	4	5	6
1	N_1	N_2	N_3	N_4	N_5	N_6
96						

Grouping of parameters	Functional
(1 2 3 4 5 6)	0.9802
(1) (2 3 4 5 6)	0.9542
. . .	. . .
(1) (2) (3) (4 5 6)	0.7401
(1) (2) (3 4) (5 6)	0.7098
. . .	. . .
(1) (2) (3) (4) (5) (6)	0.7614

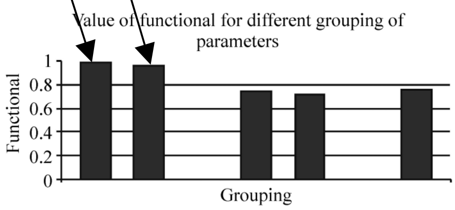

Fig. 1 Optimum grouping of parameters

	Ecological c.	Sum of em.	Humus	Sum	Silt	Ni total
1	1.1 (21) 2.2381 0.1814	2.1 (48) 2.0000 0.0000	3.1 (24) 3.7830 3.8971	 24.0500 42.2300	4.1 (23) 19.4130 27.7107	 35.9130 75.9055
	1.2 (19) 2.5263 0.5651		3.2 (24) 4.0328 4.0952	 33.4542 89.5275	4.2 (26) 24.8231 48.5418	 42.7308 168.5814
	1.2 (22) 2.7727 0.9938	2.2 (34) 1.9630 0.0357	3.3 (27) 5.0431 5.7509	 34.0926 153.5451	4.3 (27) 23.1185 35.4548	 46.2222 370.6173
	1.3 (19) 2.9474 1.3130					
96	1.5 (16) 3.2667 0.8622					

Fig. 2 Map of clusters

④ Definition of threshold values of physical and chemical parameters for forecast the concentrations of heavy metals. The threshold values physical and chemical parameters were found from theory of fuzzy sets. As shown from Fig. 3, the belong functions were constructed for physical and chemical parameters from one group with heavy metal. For threshold values of parameters are given forecast intervals for an estimation of the concentrations of heavy metals.

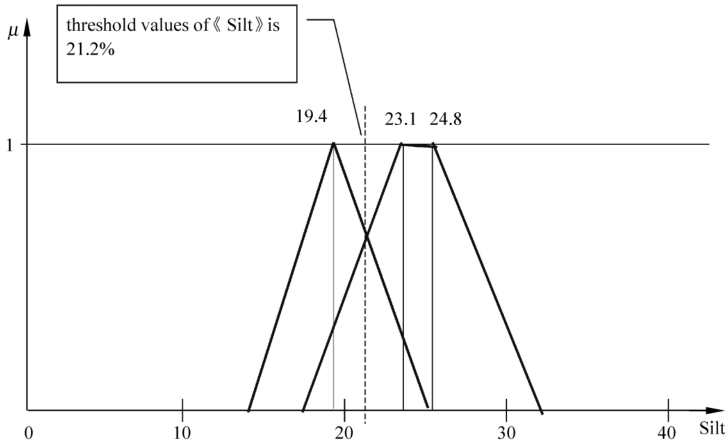

Fig. 3 Threshold value of "Silt" for Ni (total form)

Thus, if the value silt less than 21.2 % forecast interval of Ni total is within the limits of (35.8±8.7) mg/kg, it is more than 21.2 % (46.2±19) mg/kg.

The concentrations of any heavy metal can be calculated the same way.

2 Software of data soil grouping for forecast the concentration of heavy metals

The software on PC was written on Visual FoxPro 5.0 for Windows.Result of work of a program complex are the Tables, which contain the values of functionals of quality of splitting of an initial matrix for different groupings of parameters, quantity of clusters and groups of parameters, average and standard deviation for each parameter cluster.

3 Application of method on an example of Predvolgie of Tatarstan Republic

The method was applied for the data on concentrations of heavy metals in soils of Predvolgie of Tatarstan Republic. A the results the heavy metal is in one group with a physical and chemical parameters of soil. For example, one group include Ni (total and soluble form), oozy fraction and antropogeneous influence (ecological conditions). So, there is the connection of Ni (total and soluble form) and Cr (soluble form) with oozy fraction; Cu and Mn (total form) with oozy fraction, humus and sum of the absorbed bases; Cu (soluble form) with humus; Mn (soluble form) with oozy fraction and humus; Pb (total form) with the contents humus and sum of the absorbed bases; Pb and Zn (soluble form) with oozy fraction and sum of the absorbed bases; Zn (soluble form) with oozy fraction and sum of the absorbed bases.

On values of parameters including in one cluster, it is possible to determine value of any parameter from this cluster, that allows to forecast results on soil with known oozy fraction and antropogeneous influence.

Forecasted intervals of the contents of heavy metals are submitted in the Table.

Physical and chemical parameters	Heavy metal	Value of parameter	Forecasted intervals
Silt	NiT	<= 21.2 %	35.8±8.7 mg/kg
		>21.2 %	46.2±19 mg/kg
Silt	NiS	<= 21.2 %	11.7±3.2 mg/kg
		>21.2 %	14.1±5.3 mg/kg
Humus	CuT	<= 4.2 %	21±4 mg/kg
		>4.2 %	23.5±5.7 mg/kg
Humus	CuS	<= 3.9 %	5.3±1.1 mg/kg
		>3.9 %	6±1.6 mg/kg

Continue

Physical and chemical parameters	Heavy metal	Value of parameter	Forecasted intervals
Sum of the bases	MnT	<=30 mg·ekv/100g	128.7±30 mg/kg
		>30 mg·ekv/100g	141.5±55 mg/kg
Silt	MnS	<=22.5 %	137.4±32 mg/kg
		>22.5 %	153±63.4 mg/kg
Humus	PbT	<=4.1%	11.4±2.1 mg/kg
		>4.1%	13.1±2.6 mg/kg
Silt	PbS	<=23.4 %	2.1±1.4 mg/kg
		>23.4 %	2.9±1.8 mg/kg
Sum of the bases	ZnT	<=28.5 mg·ekv/100g	25.5±5 mg/kg
		>28.5 mg·ekv/100g	29.2±7.6 mg/kg
Silt	ZnS	<=23 %	5.6±1.6 mg/kg
		>23 %	7,2±2 mg/kg
Silt	CrS	<= 22 %	5.6±5.5 mg/kg
		>22 %	8.65±7.95 mg/kg

As visible from table, forecasted intervals for Ni (total form) is (35.8±8.7) mg/kg if the concentration of silt in limits or less or equal 21.2 %.

This results characterises a soil of Predvolgie of Tatarstan Republic by heavy metals as “background”.

4 Conclusions

Software of the method of data soil grouping by heavy metals allows easy to make a preliminary conclusions about significant pollution of a soil of any regions.

References

Braverman E., Muchnik I. 1983.Structural methods of processing of the empirical data. Nauka. p.464.

Koroleva T., Zakirov A., Frolova L. 2000. Use of the guarantee moment of a stop in tasks clusterisation of the ecological data. the Bulletin of the Tambov University. Natural and engineering science. Issue.5. N.5. p. 604-606.

Zaks C. 1975. Theory of statistical conclusions. Mir. p. 686-717.