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DISTRIBUTION OF ELEMENTS IN THE SOILS OF THE ZERAVSHAN VALLEY

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Annotation

The article discusses the results of studying the macro- and microelement composition of the soils of the cities of Samarkand, Navoi, Bukhara and agricultural areas of these regions. It has been established that, in the soils of agricultural areas, due to the influence of two mutually imposing factors - natural and man-made (fertilizers), there is a noticeable change in the ratio of elements and groups of rare earth elements. In the literature, data on the elemental composition of the soils of the studied territories are practically absent.

Keywords: Anthropogenic Factor, Gamma-Spectrometric Information, Standard Samples, Fertilizers, Pesticides, Industrial Pollution, Humus Content, Standard Deviation, Biostimulants.

INTRODUCTION

Soil is the surface layer of the earth's crust resulting from the impact of water, air and organisms on rocks. The composition of soils largely depends on their nature. The digestibility of trace elements from soils by plants depends on many factors, mainly depends on the alkalinity of the soil: for most elements, the digestibility of metals decreases with increasing alkalinity of the medium (pH).

With the growth of scientific and technological progress, the role of the anthropogenic factor in changing soil properties and soil-forming processes has increased significantly. The problem of diagnosing the effects of chemical influences on the soil by the introduction of fertilizers, pesticides and industrial pollution is currently becoming particularly relevant. The development of environmental protection measures is possible only as a result of a correct assessment of soil contamination [1].

When sampling soils, the location, number and type of sampling sites are determined by the local topography, the purpose of the study, the substance being analyzed and the proximity of the location to the sources of pollution. Since soil characteristics can vary greatly over a relatively short distance, it is sometimes recommended to make a “grid-averaged” selection. The number of samples and the density of the sample depend on the uniformity of the matrix and the purpose of the study. As a rule, to obtain good statistics and reduce costs, it is enough to use combined selection. When interpreting the data obtained, the following factors should be taken into account: relief, soil type, land use, chemical additives (fertilizers and pesticides) and the type of soil cover. The equipment used for sampling from the surface includes shovels, shovels and trowels, and various drilling devices are used for sampling from depth.

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Materials and methods. In our research, we limited ourselves only to considering the upper soil horizon of 0-5 cm, which can also serve as a source of pollution of the atmosphere, surface waters and agricultural products with trace elements and their compounds. In cities, samples were taken near stationary posts of the hydro meteorological center. In rural areas, samples were taken mainly in cotton-growing areas and farms growing wheat, alfalfa and grapes in addition to cotton.

After sampling, the samples were averaged, cleaned of coarse-grained fraction (small stones, plant residues) by sieving through a sieve and dried at a temperature of 105-110 ° C. 50-100 mg of soil samples were used for analysis. Then the soil samples were sealed in plastic bags and, together with the standards, were placed in an aluminum pencil case for irradiation in the channel of the VVR-SM reactor. Accumulations and processing of gamma-spectrometric information were carried out on an installation containing two spectrometric paths with Ge (Li) detectors with a volume of 80 cm3 and a mini-computer ISKRA-226 using the SOSNAA program [2]. The correctness of the analysis was controlled by parallel irradiation and comparison of standard soil samples (SP1-SP3) and international standard samples (EOP, ENO) [3]. The standard error in the element-definition was 5-20% for various elements.

The studied soils relate mainly to typical serozems. The alkalinity of the medium (pH) ranged from 8.1 to 8.8 for irrigated soils of the Samarkand region: on average 8.6; humus content from 0.6 to 1.7%; on average 0.95%; alkalinity of soils of the Navoi region are from 8.1 to 8.8; on average 8.45; humus content from 0.6 to 1.2%; on average 0.3%. In the soils of the Bukhara region, the pH value ranged from 8.2 to 8.8; on average, 8.4; humus content from 0.6 to 1.1%; on average, 0.83%.

RESULTS AND DISCUSSIONS

Figure 1 shows data on the distribution of average, maximum and minimum concentrations of elements in the studied soils of cities and rural areas of Samarkand, Navoi and Bukhara. There are also values of σr – the standard deviation, which determine the degree of dispersion of the observation around the average value.

As can be seen, there is some difference in the composition of the soils of both cities and agricultural areas. The content of Au, Se, Sb is comparatively higher in the soils sampled in Samarkand, Zn, Hg, Sb and U in Navoi, As, Vg, Hg and Au in Bukhara. These differences are due to both the composition of the soil-forming rocks of the area and the contribution of specific man-made emissions from enterprises operating in these cities.

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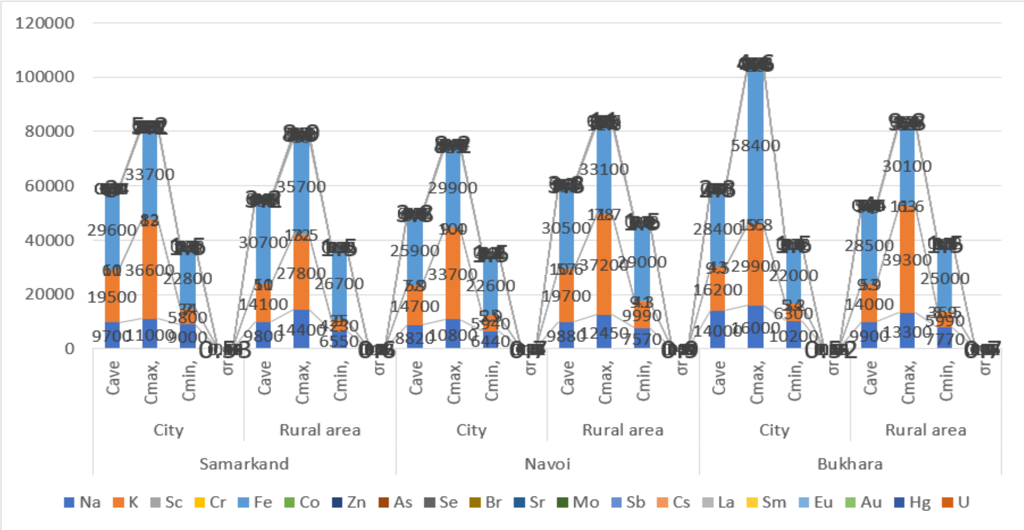

Figure 1: Distribution Of The Content Of Elements In The Soils Of The Zeravshan Valley, mg/kg

Figure 2 shows the values of the enrichment coefficients (CO), which characterize the features and differences in the composition of the soils of specific regions, compared with the earth's crust. For a large group of elements, such as Na, K, Ca, Fe, Co, Sr, Mo, Sm, Eu, their content in the studied soils is at or below the average content in the Earth's crust (Clark). The contents in r, Zn, Sb, U and Au are increased compared to Clark. The highest content, in comparison with Clark, in all studied soils was noted for As, Se and Hg. It was interesting to compare the results of soil analyses of agricultural areas and cities (Fig. 3). Compared to cities, the soils of irrigated lands are significantly enriched with Zn and Hg (Samarkand region.), Sr (Navoi region) and U (Bukhara region). The soils of the city of Samarkand are enriched with Sb, Bukhara - Na, Hg and As, Navoi - As.

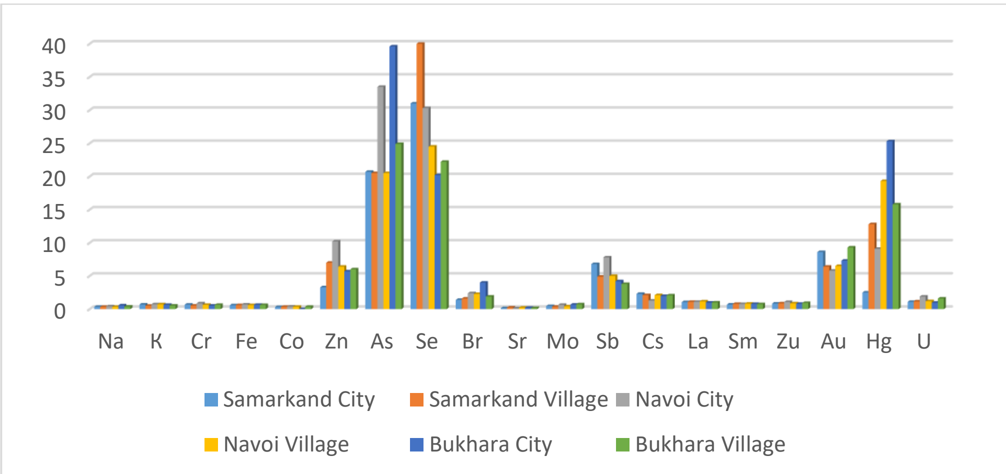

Figure 2: Coefficients of Element Enrichment in Soils of the Zeravshan Valley

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For most elements in soils, the maximum permissible concentration (MPC) has not yet been developed. Therefore, when assessing soil contamination with toxic elements for which MPCs have not been developed, pollution levels were compared with the natural local background level. We have taken data on the Zaamin Nature Reserve as a local background level of the content of elements in soils. Figure 3 shows the results of comparing the average concentrations of elements in the soils of the studied cities with data on the composition of the soils of the Zaamin Reserve.

Background, mg/kg												
Na	Sc	Cr	Fe	Co	Zn	Se	Br	Sb	Cs	la	Sm	Hg
2400	11	74	36000	13	170	1,2	3,4	1,9	4,7	29	8,2	0,91

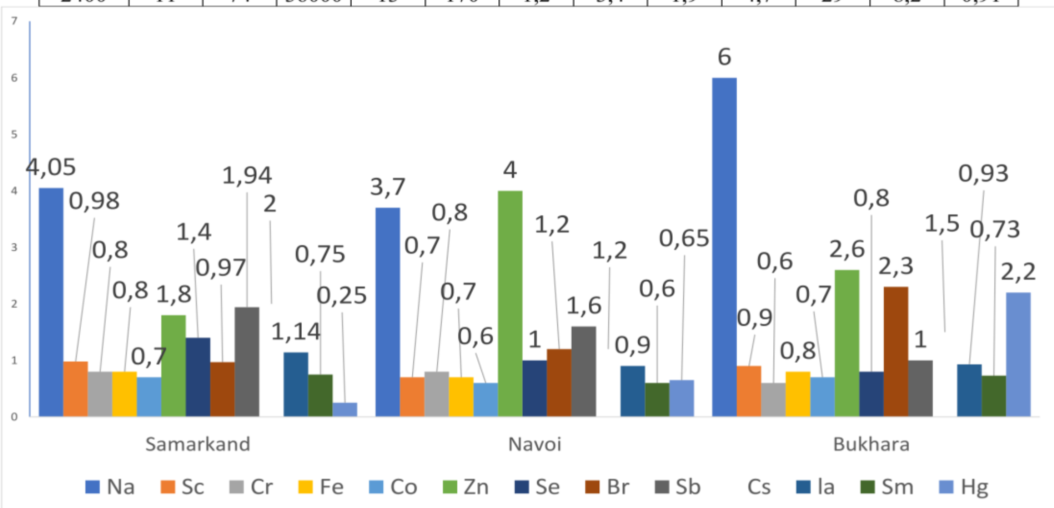

Figure 3: The Ratio of the Concentration of Elements in the Soils of Polluted Territories to the Background

As can be seen, there is a slight increase in the average content of Na, Zn, Sb and Cs in the soils of the studied cities compared to the soils of the reserve. Moreover, there are noticeable differences in the ratios of concentrations of elements in the soils of individual cities. In particular, the soils of Navoi are comparatively enriched with Zn and Cs, Samarkand Se and Sb, Bukhara Hg, Vg and Na, which, apparently, is due, as mentioned above, to the peculiarities of the composition of soil-forming rocks and the influence of man-made factors in the cities studied. In comparison with the soils of the reserve, there is a slight decrease in the average concentrations of Sc, Sg, Fe and Co, that is, elements that seem to have a typical natural origin in the soils of the studied cities.

The geochemical criterion for the relationship of elements in different environments can be the value of the correlation coefficients between them. Due to the limited scope of the article, some tables of the coefficients of paired correlations between the concentrations of elements are given below. These tables differ somewhat from the widely used standard triangular matrices. Here the elements are divided into two (equal in this case) groups, and the correlation coefficients are also presented in two (sub) matrices. In the first submatrix, the correlation

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coefficients between the elements of the first group are shown above its diagonal, and below – between the elements of the second group. And the correlation coefficients between the elements of different groups are given in the second submatrix.

Such a representation, in addition to its compactness, will be more informative if the elements are divided into groups according to a certain attribute, for example, according to the degree of their connection with each other. This feature is used in the tables being conducted. Namely, the first group includes the most closely related (collectively) elements, and the second group includes the rest. However, within both the first and second groups, the elements are ordered by the degree of connection of the element with the elements of this group (in the first submatrix) or with the elements of another group (in the second submatrix). Note that the average values of the sums of the absolute values of the coefficients of the paired correlation of the element with the elements of this and other groups, respectively, are used as measures of the relationship of the element with the elements of this or another group. The elements were divided into groups and their ordering was carried out using a program developed by us for this purpose in the Fortran-IV language.

In Tables 1, 2, using the example of the soils of the city of Samarkand and rural areas of the Samarkand region, the data of correlation analysis between pairs of elements are presented. In the tables, significant (at the level of α=0.05 [4]) correlation coefficients ($r > 0.36$) are underlined.

Similar results were obtained for other studied soils.

Table 1: Coefficients of Paired Correlations between Elements in the Soils of the City Of Samarkand

		Sc	Cd	Cr	Fe	Au	Hg	As	Element
		0.94	0.97	−0.81	0.82	0.81	0.71	−0.69	Mo
Se	0.61	■■■	0.94	−0.91	0.63	0.86	0.54	−0.70	Sc
Sm	-0.52	-0.37	■■■	−0.79	0.74	0.89	0.61	-0.54	Cd
Eu	0.28	0.59	-0.37	■■■	-0.55	−0.82	-0.49	0.59	Cr
Sb	-0.50	−0.65	0.01	0.16	■■■	0.48	0.95	−0.68	Ee
U	0.02	−0.71	-0.14	-0.37	0.61	■■■	0.39	-0.24	Au
La	-0.20	0.07	0.74	0.32	0.09	-0.33	■■■	−0.66	Hg
Co	-0.27	0.01	-0.51	0.63	0.61	0.01	-0.18		
Element	Zn	Se	Sm	Eu	Sb	U	La		

Element	Eu	Zn	U	Sm	Sb	Se	Co	La
As	-0.41	−0.83	-0.14	0.79	0.18	-0.60	-0.14	0.40
Mo	0.57	0.61	0.46	-0.59	0.38	0.13	0.39	-0.12
Fe	0.49	0.58	-0.10	−0.64	0.11	0.57	0.55	0.02
Hg	0.83	0.70	-0.27	-0.06	-0.16	0.70	0.36	0.02
Cd	0.50	0.48	0.55	-0.48	0.50	-0.04	0.38	-0.05
Sc	0.34	0.66	0.61	-0.46	0.31	0.02	0.11	-0.10
Au	0.29	0.37	0.59	-0.07	0.49	-0.26	0.08	0.22
Cr	-0.36	−0.66	-0.44	0.16	-0.18	-0.14	0.11	-0.25

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As follows from the data in Table 1, in the surface layer of urban soils, Sc, Cd, Sg, Fe and Au had close correlations with each other. For a large group of elements. Co, La, U, Sb, Eu, Sm and Se, the number of significant correlations between themselves and with other elements is noticeably less. It is incomprehensible that there are no significant correlations between rare earth elements (REE), especially between La and Eu, if it is not explained by errors in the determination of europium. Thus, deep ecological disturbances in natural ratios and concentrations of elements occur in the surface soil layer of cities due to anthropogenic emissions [5]. In general, the violation of correlations between pairs of elements is more clearly expressed in the soils of irrigated lands (Table 2).

Table 2: Coefficients of Paired Correlations between Elements in Soils of Irrigated Lands of the Samarkand Region

		Cd	Sc	Mo	Sm	Au	Hg	Sb	Element
		0.35	0.64	0.25	0.47	0.03	-0.30	−0.60	Zn
Se	0.19	■■■	0.30	0.45	0.09	0.70	-0.30	-0.06|	Cd
Fe	-0.17	−0.40	■■■	0.07	0.44	0.14	−0.40	-0.24	Sc
As	0.28	-0.08	0.27	■■■	0.45	0.39	0.14	-0.26	Mo
Eu	-0.09	−0.43	0.14	0.14	■■■	0.15	-0.10	-0.26	Sm
Cr	-0.12	-0.15	0.26	-0.07	0.10	■■■	0.20	-0.01	Au
La	-0.34	0.07	0.07	-0.05	-0.05	0.02	■■■	0. 02	Hg
U	0.19	-0.02	0.01	-0.17	0.10	-0.09	0.02		
Element	Co	Se	Fe	As	Eu	Cr	La		

Element	U	Fe	La	Cr	As	Co	Se	Eu
Sm	0.28	0.30	0.15	-0.20	0.07	0.13	0.12	0.02
Sc	-0.01	0.37	0.22	0.05	0.28	0.13	-0.01	-0.05
Cd	-0.20	0.14	0.20	0.18	0.02	-0.03	-0.15	-0.15
Au	-0.30	0.02	0.12	0.28	0.03	-0.06	-0.17	0.03
Mo	0.10	0.12	0.10	0.28	-0.14	0.03	0.10	-0.03
Zn	0.06	0.06	0.21	0.03	0.02	0.23	0.14	-0.03
Sb	-0.15	-0.06	0.07	-0.04	0.23	-0.10	0.03	-0.10
Hg	0.07	-0.07	-0.06	0.06	-0.12	-0.09	0.05	0.01

According to the statistical yearbooks of the Republic over the past 20 years, an average of more than 6,500 kg of phosphate fertilizers have been applied to each hectare of the sown area of the republic. The raw materials for them are natural concentrates of phosphorites and apatites of some deposits containing an increased amount of certain elements. Phosphates on average contain 0.005-0.02% U, 0.1-1% REE and other elements [6].

A characteristic feature of soil contamination by elements and rare earth elements is a change in the ratios of elements and the REE group, which can be seen from the data of correlation analysis (Table 1, 2). It seems to us that in the soils of agricultural areas, due to the influence of two mutually imposed factors - natural and man-made (fertilizers), there is a noticeable change in the ratio of elements and groups of REE.

To assess the contribution of phosphorus fertilizers, Table 3 shows data on the content of elements in phosphorites and phosphorus fertilizers [6].

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Table 3: The Content of Elements in Phosphorites and Phosphate Fertilizers, Mg/Kg [6]

Элемент	Фосфориты		Фосфатные удобрения
	By Bowen	По Трудингеру	
As	30	0.4-188	2-1200
B	<50	3-33	5-115
Cd	0.01-35	1-10	-
Cl	100	9-85	20
Co	<3-5	0.6-12	1-10
Cr	2-1000	7-1600	66-245
Cu	100	0.6-394	1-300
Fe	31000	-	8500-15500
Hg	0.2	10-1000	0.01-0.2
I	0.8-280	0.2-280	-
La	-	7-130	-
Mn	30	1-10000	40-2000
Mo	0.03	1-138	0.1-60
Ni	<2-1000	2-30	7-32
Pb	2-14	<1-100	7-225
Sb	0.2-7	1-10	-
Se	-	1-10	<0.5
Sn	0.2	10-15	3-4
Ti	600	100-3000	-
U	90	8-1300	-
V	300	20-500	2-180
Zn	300	44-345	50-1450
Zr	30	10-800	50

In addition, most of the natural reserve of elements in soils is inaccessible to plants, while elements and REE are introduced together with fertilizers in more accessible, soluble forms [7].

Thus, the excessive chemicalization of agriculture, along with a positive effect, causes negative consequences – a violation of the established cycles of turnover of elements and the ecological balance of natural and anthropogenic systems. In this regard, the assessment of the amount of elements coming with fertilizers is also important for understanding the mechanism of formation of soil composition, especially since, as it was shown [8], pollution of surface reservoirs of the republic is largely associated with the flushing and leaching of elements and their compounds from irrigated lands.

In conclusion, it should be noted that in soils it is somewhat more difficult to identify trends in the levels of pollution by elements, since this requires long-term observation.

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CONCLUSIONS

1. The obtained data, using correlation analysis, allow us to evaluate some physico-chemical factors of the formation of the elemental composition of the studied soils, and more objectively substantiate the conclusions of agrochemical and environmental studies;
2. The constantly increasing rates of application of mineral fertilizers, biostimulants and chemical agents for plant protection in agriculture require periodic comprehensive study and assessment of the composition of soils for toxic elements and their compounds.
3. In the future, based on the above data, it is necessary to take into account the possible accumulation by agricultural crops of not only N, P, S and pesticides, but also trace elements when applying phosphorus-containing fertilizers to the soil;
4. It should also be taken into account that soil pollution can lead to further pollution of other media, in particular, atmospheric air, surface reservoirs and groundwater in the region.
5. The data obtained and their interpretation give general ideas about the current state of soil pollution of the studied territories by elements and can be recommended for pollution control and protection of urban soils.

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