

The Patterns of Spatial and Temporal Distribution of Element Concentrations in Atmospheric Aerosols of the Cities in the Zeravshan Valley

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ABSTRACT

The patterns of spatio-temporal distribution of element concentrations in atmospheric aerosols of large cities in the Zeravshan Valley have been studied. The obtained results are explained using statistical methods, taking into account meteorological parameters and the location of industrial enterprises in these cities. The spatial and time distribution of urban atmosphere aerosols of Samarkand, Bukhara and Navoi was investigated. The derived data was described in the frame of statistical methods accounting of meteorological parameters and industry placement.

Keywords: Atmospheric aerosols, Zeravshan Valley, spatial distribution, temporal distribution, element concentrations, statistical methods, meteorological parameters

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Introduction. The problem of studying the composition and patterns of spatio-temporal and concentration-size distributions of atmospheric aerosols becomes particularly relevant due to the increasing level of environmental pollution caused by human activities: the growing number of vehicles, production capacities, etc. Aerosols released into the air as a result of such activities can cause significant harm to flora and fauna, as well as lead to human diseases [1].

In recent years, nuclear-physical methods of analysis have become increasingly widely used in the field of ecology as well [2]. This is particularly due to the fact that the nationwide environmental monitoring and pollution control service operating

in our country monitors atmospheric air pollution in cities and industrial centers mainly for a limited range of ingredients (dust, SO₂, NO₂, CO, etc.). For most cities, data on the elemental composition of atmospheric aerosols, especially regarding heavy metals, are insufficient. Among such cities are the large cities of the Zeravshan Valley-Bukhara, Samarkand, and Navoi. This region is characterized by the presence of extensive biogeochemical areas, polymetallic deposits, developed mining, mineral processing, chemical and mechanical engineering industries, agriculture, as well as a large fleet of motor vehicles.

For an objective assessment of the atmospheric air quality in the cities of Bukhara, Samarkand, and

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Navoi, as well as for selecting priority ingredients to be monitored by the network of existing services, obtaining data on the content and distribution of heavy metals in these cities is of great interest.

This paper presents the results of a study on the concentrations of elements, including heavy metals, in atmospheric aerosols of these cities and the patterns of their spatio-temporal distribution. The concentrations of elements were determined using a highly sensitive instrumental neutron activation analysis method [2].

Materials and Methods. Atmospheric aerosols were collected daily on AFA-KhA filters (except Sundays and public holidays) over the course of a year at the most characteristic reference monitoring posts of the Hydrometeorological Service: in Samarkand at Post No. 2 (hereinafter referred to as S2), in Bukhara at Post No. 1 (B1), and in Navoi at Posts No. 3 (N3) and No. 2 (N2). With the exception of Post No. 3 in Navoi, all other posts are located in close proximity to roads.

In order to study the influence of meteorological factors on the concentrations of the studied elements on the days of aerosol sampling, the main meteorological parameters such as temperature, humidity, air pressure, wind speed and direction, amount of precipitation, etc., were recorded. For comparison and identification of genetic relationships, data from the Hydrometeorological service [3] on the main gaseous ingredients such as SO₂, CO, and NO₂ were used.

Using an aspiration device, approximately 7–10 m³ of air was passed through AFA-KhA filters. Then, under laboratory conditions, the filters were dried, sealed in polyethylene bags, and placed together with standards into an aluminum container for irradiation in the channel of the VVR-SM reactor.

The accumulation and processing of gamma-spectrometric information were carried out using a setup comprising two spectrometric channels with Ge(Li) detectors of 80 cm³ volume and an ISKRA-226 minicomputer, utilizing the SOSNAA software [4]. The accuracy of the analysis was monitored by parallel irradiation and comparison of standard air samples (SV), water samples (SOV1–SOV5), soil samples (SP1–SP3), and international standard reference materials (EOR, ENO) [5]. The standard error for elemental determination ranged from 5–20% for various elements.

Statistical processing of the data was performed on a personal computer using the standard

STATGRAPHICS software [6]. The application of statistical methods makes it possible to increase the information content of observational data on elements, identify the main factors influencing the processes of distribution and dispersion of elements in atmospheric aerosols, and, in some cases, determine their quantitative characteristics.

In particular, the necessity of applying analysis of variance in ecological issues is dictated by the fact that it allows for a statistically justified comparison of data from different cities, as well as for different periods of the year corresponding to different levels of influence of certain factors, thereby avoiding unfounded conclusions about the ecological situation and its dynamics.

Results and Discussion. A preliminary analysis of the distribution of element concentrations using the Kolmogorov–Smirnov criterion showed that the distribution in all cases was close to lognormal. Subsequently, outliers (suspicious observations) were removed from the obtained (log-transformed) data using Thompson's criterion [7]. The number of excluded observations was typically 5–6% of the total sample for various elements. The data were then subjected to analysis of variance (ANOVA) [6,8] in order to detect significant differences in the data for different cities, as well as for different periods of the year corresponding to different levels of influence of certain factors.

The fundamental idea of analysis of variance is that the variance of a random variable (in this case, the concentration of elements) is considered decomposable into component parts caused by the influence of certain factors (A, B, C, etc.) individually and jointly on the given variable, as well as into residual variance caused by unaccounted and random factors:

$$S^2 = S_A^2 + S_B^2 + S_C^2 + \dots + S_{AB}^2 + S_{AC}^2 + S_{BC}^2 + \dots + S_X^2 \quad (1)$$

These components of the total variance can be grouped into three categories corresponding to the so-called main effects of factors (S_A^2 , S_B^2 , S_C^2 etc.), the interaction of factors (S_{AB}^2 , S_{AC}^2 , S_{BC}^2 и т.д.) and finally, the residual variance (S_X^2). The significance of the influence of each factor (or their combined influence) on the variable of interest can be assessed using the F-ratio, which represents the ratio of the corresponding variance component to the residual variance.

$$F_A = \frac{S_A^2}{S_X^2}, \quad F_B = \frac{S_B^2}{S_X^2}, \quad F_{AB} = \frac{S_{AB}^2}{S_X^2} \quad (2)$$

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To perform analysis of variance, the sample data are divided into groups. Within each group, only a specific value (level) of a factor is operative. Each such group can, in turn, be subdivided into groups according to the levels of another factor, and so on. The variance components corresponding to the main effects are determined as follows:

- a) the average values of element concentrations are calculated for each level of the factor;
- b) the sum of squares of the deviations of these averages from the overall mean is determined;
- c) the sum of squares divided by the degrees of freedom of the factor, which is one less than the number of different degrees of the factor.
- d) the resulting value gives the corresponding component of variance.

The variances resulting from the interaction of factors are calculated in a similar way, where the degree of freedom is equal to the product of the degrees of freedom of the factors. In our research, we will limit our research to two-factor analysis. In this case, S_{AB}^2 can be easily determined by subtracting S_A^2 and S_B^2 from the so-called intergroup variance of means, which is the variance of the means of all distinguished groups, the number of which is equal to the product of the numbers of levels of the factors. In this regard, we note that the residual variance is also called the within-group variance. It is defined as the ratio of the sum of the squared deviations of the within-group observations from the group mean to the degrees of freedom, which is equal to the total number of observations minus the number of all groups.

The obtained F-ratio values are compared with tabulated values for the given degrees of freedom of the numerator and denominator, as well as the significance level (most often the significance level is taken as $\alpha = 0.05$ or $\alpha = 0.01$). If the calculated F-ratio is greater than the tabulated F-critical value, then it can be concluded that the variation in means is not random but rather a consequence of the influence of this factor or the combined influence of factors (with the probability of error not exceeding the accepted significance level). Furthermore, the critical values of significance levels can be used to judge the relative degree of influence of factors on the observed variable.

It should be noted that in the analysis of variance, the exact levels (“values”) of the influence of factors are not directly used in the calculations, and

they usually have a qualitative nature and serve only to differentiate data groups.

In the presence of factors whose levels can be represented quantitatively, such as meteorological parameters, and which also correspond precisely to the time of sample collection, a natural desire arises to obtain not a qualitative but rather a quantitative relationship between the concentrations of elements and the values of these parameters.

An approximate but sufficiently clear relationship can be obtained within the framework of linear regression analysis. Table 1 presents the coefficients of the regression equations that we obtained using stepwise multiple linear regression [6,9], where the independent variables were the main meteorological parameters – air temperature, humidity, pressure, and wind speed.

$$lgC_{elem.} = b + t \cdot lg(T + 25) + e \cdot lgE + p \cdot lgP + v \cdot lg(V + 1) \quad (3)$$

where b is the free term of the equation, T-is the air temperature (°C), P-is the air pressure (gPa), E-is the relative humidity of the air (%), and V-is the wind speed (m/s)

As can be seen from Table 1, wind speed is significantly related to element concentrations only for the city of Bukhara, and element concentrations increase with increasing wind speed. An inverse relationship is observed only for Br and Sb. Increased wind speeds lead to dilution of the air in this area and a decrease in the concentration of elements of local origin.

Table 1.
Coefficients of meteorological parameters in the regression equations for element concentrations

element	C2					H2					B1				
	b	t	e	p	v	b	t	e	p	v	b	t	e	p	v
Na	3.7	-	-0.4	-	-	2.92	-	-	-	-	4.6	-0.9	-	-	-
Se	-1.1	1	-	-	-	0.9	-	-0.3	-	-	0.7	-0.3	-	-	0.3
Cr	-49	-	-	17	-	-66	1.4	-	22	-	0.6	-	0.5	-	-
Fe	2.9	0.8	-	-	-	4.4	-	-0.3	-	-	3.15	-	-	-	-
Co	1.2	-	-0.4	-	-	0.9	-	-0.2	-	-	0.5	-	-	-	0.2
Zn	-46	-	-0.4	17	-	1.4	0.7	-	-	-	-33	-	-	12	-
Br	2.05	-	-	-	-	2.14	-	-	-	-	-56	1.3	-	19	-0.3
Sb	-0.3	0.8	-	-	-	0.91	-	-	-	-	0.6	0.3	-	-	-0.3
Cs	1.2	-	-0.5	-	-	0.8	-	-0.3	-	-	0.9	-0.4	-	-	-
La	0.1	0.6	-	-	-	1.4	-	-0.3	-	-	1.4	-0.4	-	-	0.3
Sm	1	-	-0.4	-	-	0.9	-	-0.6	-	-	-55	-	-	18	0.5
Eu	1.87	-	-	-	-	2	-	-0.2	-	-	1.3	-	0.2	-	0.2
Au	2.2	-0.8	-	-	-	-163	1.2	-	54	-	2.17	-	-	-	-
Hg	85	-1.2	-0.7	-27	-	62	-	-	-21	-	0.82	-	-	-	-
Th	2.7	-	-1.5	-	-	-92	1.6	-	30	-	0.1	-	-	-	0.3
dust	-148	1.3	-	50	-	61	-1.1	0.3	-19	-	1.1	-	0.2	-	0.3

For element concentrations (except for Cr and Eu) in atmospheric aerosols of the city of Bukhara, there is practically no dependence on air humidity. This can apparently be explained by the relative dryness of the air in this city compared to the air in the cities of Navoi and Samarkand [10,11] (In winter, the relative air humidity was 66% in

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Bukhara, 75% in Samarkand, and 78% in Navoi). In the cities of Navoi and Samarkand, a completely explainable pattern of dependence of concentrations of most elements on air humidity is observed, namely, their decrease with increasing air humidity. At the same time, the absence of dependence on wind speed for all elements in these cities seems difficult to explain. This may be due to the linearity of the approximation. The reason may also lie in the fact that parameters such as wind speed and direction are very variable and their instantaneous values are determined, as a rule, very approximately, and they may indeed differ significantly from their average values over a certain period of time (for example, over half an hour), during which this level of atmospheric pollution is actually formed.

Thus, the influence of wind speed and direction on the concentrations of dust and elements can apparently be detected not by their instantaneous values, but by average values over a relatively long period. In this regard, we used average monthly wind speeds and directions (Table 2).

The prevailing wind direction for the month was taken as the resultant wind direction for that period with a stability of at least 0.5. In this case, similar wind directions were combined into one class. Resultant wind directions with stability less than 0.5 were considered a mixture of winds of different directions and were combined into another class.

Table 2.

Average monthly wind characteristics in the cities of the Zeravshan Valley over the studied period

Month	Average speed, m/s				Prevailing wind direction				Stability of the prevailing wind			
	S2	N3	N2	B1	S2	N3	N2	B1	S2	N3	N2	B1
Sept.	2.8	2.2	2.5	3.9	SE	SE	SE	N	0.44	0.50	0.58	0.89
Oct.	2.5	2.0	2.2	3.6	SE	E	SE	N	0.36	0.17	0.39	0.58
Nov.	2.5	2.7	2.2	3.8	SE	E	E	SE	0.54	0.50	0.52	0.20
Dec.	2.9	2.8	1.9	3.9	SE	SE	E	E	0.43	0.50	0.35	0.10
Jan.	2.5	2.3	2.1	4.2	S	SE	E	NW	0.36	0.27	0.27	0.05
Feb.	2.6	2.3	2.3	4.5	SE	E	E	SE	0.50	0.56	0.56	0.16
March	3.1	2.4	2.4	4.0	SE	SE	SE	N	0.42	0.40	0.40	0.29
Apr.	3.4	2.6	2.6	4.5	S	E	E	N	0.30	0.27	0.27	0.51
May.	2.6	2.5	2.5	4.3	SE	E	E	N	0.45	0.25	0.25	0.34
June.	2.9	2.6	2.6	4.6	E	SE	SE	N	0.44	0.52	0.52	0.89
July.	2.4	2.8	2.8	4.5	E	SE	SE	N	0.51	0.72	0.72	0.92
Aug.	2.2	2.1	2.1	4.4	E	N	N	N	0.53	0.53	0.53	0.86

In Bukhara, during the relatively warm period of the year, northern winds clearly prevail, with stability approaching 1 in some months, so the above remark is least applicable to the results for the city of Bukhara. For the cities of Samarkand and Navoi, eastern and southeastern winds are quite stable. Winds were also divided into two classes by speed: above and below the annual

average. The average monthly wind speeds over the studied period were 2.2–3.4 m/s in Samarkand, 3.6–4.6 m/s in Bukhara, and 1.9–2.8 m/s in Navoi. Since we had data for the entire year, seasonality can be considered the most natural factor influencing element concentrations, with two levels: the warm period (above the annual average temperature) and the relatively cold period (below the annual average temperature). Another important factor is the difference in the location of stationary sampling posts, the specific conditions in the immediate vicinity of the posts: the presence of industrial enterprises, highways, etc.

To study the significance of the site factor, samples from different sites were combined in pairs. Thus, for four sites, there are six combination options such as S2+N3, S2+N2, etc. When conducting one-way and two-way analyses of variance of element concentrations, conditional numbers were used (see Table 3) characterizing the degree of association of element concentrations with factors. The number "0" corresponds to the insignificance of the influence of a factor or the joint influence of two factors at a significance level of $\alpha = 0.05$. The remaining numbers correspond to a significant influence of factors:

$$1 - 0.05 > \alpha \geq 10^{-2}; 2 - 10^{-2} > \alpha \geq 10^{-3}; 3 - 10^{-3} > \alpha \geq 10^{-4}; 4 - \alpha < 10^{-4} \quad (4)$$

Table 3.

According to the results of the analysis of variance, the levels of correlation of element concentrations with seasonality, location of the post and their interaction

element	seasonality				site location of the sampling post				interaction									
	S2 + N3	S2 + N2	S2 + B1	N3 + N2	N3 + B1	N2 + B1	S2 + N3 + N2	S2 + N3 + B1	S2 + N2 + B1	N3 + N2 + B1	N3 + N2 + B1	S2 + N3 + N2 + B1	S2 + N3 + B1 + N2	S2 + N2 + B1 + N3	N3 + N2 + B1 + S2			
Na	4	3	3	2	4	4	4	4	1	4	4	0	0	1	4	4	4	2
Sc	4	4	0	1	0	4	4	4	4	0	0	2	0	0	4	4	4	0
Cr	0	4	1	1	0	3	1	0	0	0	0	0	0	0	4	3	4	0
Fe	4	3	2	4	1	4	4	4	4	0	2	0	1	0	0	3	0	1
Co	4	3	0	2	0	4	3	3	1	0	0	0	0	0	1	4	2	0
Zn	3	2	1	0	0	4	4	4	3	1	0	0	1	0	3	4	4	0
Br	0	0	4	4	4	1	4	4	4	4	0	4	0	0	4	4	4	0
Sb	0	3	3	1	0	1	4	4	4	3	4	4	4	0	0	4	0	3
Cs	4	4	0	0	0	4	4	4	4	1	0	1	0	0	4	4	4	0
La	4	3	0	0	0	4	4	4	4	0	4	3	0	0	4	4	4	0
Sm	4	4	0	0	0	4	4	4	4	2	2	4	2	2	3	4	4	0
Eu	0	3	0	0	0	4	4	4	0	1	3	0	0	3	1	3	0	0
Au	4	2	3	3	0	1	0	4	3	4	0	4	0	3	2	2	0	3
Hg	1	3	3	1	3	2	2	4	0	0	4	4	0	0	0	0	0	0
Th	4	4	4	4	3	4	4	4	1	2	2	0	0	4	4	4	4	2
dust	0	4	0	3	4	4	1	0	2	4	2	4	1	4	0	0	4	1

As can be seen from Table 3, Fe, Hg, Na, Th, and Au were sensitive to seasonality in most cases; for almost all sites, the average annual concentrations

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of dust, rare earth elements (REEs), as well as Sb, Br, Na, Cs, and Th differ significantly. Particularly interesting is the fact that the significance of the interaction between the factors of seasonality and site location is mainly observed for samples involving data from the city of Bukhara. This indicates that the seasonal changes in element concentrations in Bukhara differ not only quantitatively but also qualitatively from those in the other two cities of the Zeravshan Valley.

If in the last two cities a significant decrease in their concentration is observed mainly in the cold season for elements of soil origin - in Samarkand for Na, Sc, Fe, Co, Cs, Eu and Th, in Navoi (N3) for Na, Sc, Fe, Co, Cs, La, Sm and Th, in Navoi (N2) for Sc, Fe, Co, Cs, La, Sm, Eu and Th (Table 4), then in Bukhara the concentration of many elements, including mainly soil elements, increases in winter. This, at first glance, somewhat unexpected fact can be explained by the location of industrial enterprises and climatic features, including wind speeds, of these cities.

Table 4.

Values of average concentrations of elements in atmospheric aerosols of cities in the Zeravshan Valley, in ng/m³

Element	Annual average concentration				Average concentration in the warm period				Average concentration in the cold period			
	S2	N3	N2	B1	S2	N3	N2	B1	S2	N3	N2	B1
Na	1500	1060	1000	1900	1660	1190	<u>990</u>	1180	1330	920	<u>1030</u>	2600
Sc	4.0	3.2	2.7	2.9	4.4	3.8	3.0	2.5	3.7	2.6	2.4	3.3
Cr	35	33	30	30	<u>37*</u>	<u>32</u>	<u>32</u>	23	<u>32</u>	<u>34</u>	<u>27</u>	38
Fe**	176	127	115	126	186	153	123	<u>126</u>	166	100	106	<u>125</u>
Co	5.2	4.4	4.4	4.7	5.5	5.1	4.8	<u>4.5</u>	4.8	3.8	4.0	<u>4.9</u>
Zn	550	370	380	450	<u>570</u>	425	415	390	<u>520</u>	320	340	510
Br	145	40	155	170	<u>140</u>	<u>39</u>	<u>145</u>	200	<u>147</u>	<u>41</u>	<u>160</u>	130
Sb	14	6.8	10	7.5	15	5.5	<u>10</u>	<u>7.6</u>	12	8.1	<u>9.6</u>	<u>7.3</u>
Cs	3	2.4	2	2.1	3.2	2.7	2.3	1.7	2.7	2	1.8	2.4
La	15.6	11	9.3	11.2	<u>15.5</u>	12.2	10	10	<u>15.6</u>	9.4	9	13
Sm	2.5	1.7	1.3	1.5	<u>2.3</u>	2	1.5	1.3	<u>2.3</u>	1.4	1	1.7
Eu	0.9	0.7	0.6	0.7	1	<u>0.7</u>	0.6	0.6	0.8	<u>0.7</u>	0.4	0.8
Au	0.13	0.1	0.08	0.08	0.09	<u>0.1</u>	<u>0.08</u>	<u>0.08</u>	0.2	<u>0.1</u>	<u>0.08</u>	<u>0.08</u>
Hg	8	6.3	10.8	6.7	9	7.6	14	<u>6.7</u>	6.9	5	7.5	<u>6.7</u>
Th	3.6	2.5	2.1	2.5	4.8	3.1	2.4	<u>2.4</u>	2.5	1.9	1.8	<u>2.5</u>

Note:

*Concentration values of elements that did not differ significantly (according to analysis of variance at a significance level of $\alpha = 0.05$) between the warm and cold periods are underlined; **Concentration values for Fe are given in 100·ng/m³.

In the city of Navoi, as already mentioned, the prevailing wind directions are eastern and southeastern, which are not seasonal in nature.

Therefore, most industrial enterprises, including large ones, located outside the city to the west and southwest, pollute the city's atmosphere equally during both the warm and cold periods of the year, but to a much lesser extent (considering the wind rose) than might be expected. At the same time, the main sources of air pollution in the city throughout the year are enterprises such as the cotton ginning plant and the repair and mechanical plant, located on the side of the prevailing wind direction. "Purely" seasonal effects also manifest themselves in Samarkand for approximately the same reason, namely, due to a constant level of atmospheric air pollution above the seasonal background by industrial enterprises such as the "Metalworking" Production Association, the experimental mechanical plant, and the "Krasny Dvigatel" plant, which are located east and southeast of the sampling post, within the city itself. In this regard, we note (see Tables 3 and 4) that the level of air pollution with most elements (Fe, Co, Zn, Au, Sc, La, Sm, Eu, Th) in Samarkand is significantly higher than in the other two cities.

As for the city of Bukhara, here, firstly, factors such as the amount of precipitation (typically falling during the relatively cold period of the year), which is significantly lower in Bukhara (83 mm) than in the cities of Navoi (125 mm) and Samarkand (318 mm), and the average wind speed, which is almost twice as high in Bukhara compared to the other cities, should be taken into account. These circumstances favor the wind erosion of soil in Bukhara to approximately the same extent during both the warm period and the relatively cold period of the year, and significantly reduce the effect of seasonality.

Table 5.

Degrees of association of element concentrations with soil condition (dry – wet), according to the results of analysis of variance

Element	S2	N3	N2	B1	Element	S2	N3	N2	B1
Na	3	1	0	0	Cs	4	2	3	1
Sc	4	4	1	0	La	3	4	2	0
Cr	0	2	0	2	Sm	3	4	4	1
Fe	3	4	2	0	Eu	3	0	1	0
Co	3	3	1	0	Au	2	0	0	0
Zn	2	4	3	0	Hg	0	0	0	0
Br	0	0	0	0	Th	4	4	2	0
Sb	4	0	3	0	dust	1	1	3	0

Indeed, as shown by the results of one-way analysis of variance (Table 5), where soil condition (dry-wet) acted as a factor, the concentrations of all elements (except Cr, Cs, and Sm) and dust in the atmosphere of Bukhara did not differ significantly between dry and wet soils. At the same time, in the

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other two cities, the concentrations of most elements differed significantly between dry and wet soils (with element concentrations decreasing under wet soil conditions). Exceptions were Cr, Br, and Hg for Samarkand; Na, Cr, Br, Au, and Hg for post N2; and Br, Sb, Eu, Au, and Hg for post N3 in Navoi. This allows us to consider road dust as one of the main sources of the elemental composition of aerosols. We also note that the content of Br and Hg in all cases does not depend on soil condition, indicating their technogenic origin. Secondly, as already noted, in Bukhara during the warm period of the year, northern winds clearly prevail (frequency 60-70%). In late autumn and winter, the frequency of eastern and southeastern winds increases noticeably (30-35%). In this direction are located most of the industrial enterprises, including the reinforced concrete products and expanded clay plant, the building materials combine, the house-building combine, the asphalt-concrete plant, etc. Some of these enterprises significantly exceed similar enterprises in Navoi in terms of the degree of environmental pollution. (For comparison, Table 6 presents the elemental composition of aerosol emissions from the reinforced concrete products and expanded clay plant (RCPECP) in Bukhara and the Navoi Cement Plant, sampled by us from the stacks of these plants).

Table 6.

Concentration of elements in aerosol emissions from certain enterprises into the atmosphere of cities in the Zeravshan Valley, in mg/kg

Элемент	Plant RCPECP (Bukhara city)	Navoi Cement Plant	Element	Plant RCPECP (Bukhara city)	Navoi Cement Plant
Na	14300	1500	Sr	290	300
K	17500	1700	Mo	0.5	0.5
Sc	22	5.5	Sb	5	1.5
Cr	14	100	Cs	9	52
Fe	67300	23000	La	35	11
Co	24	6.5	Sm	8.5	1.5
Zn	320	555	Eu	2	0.5
As	220	25	Au	0.01	0.1
Se	2.5	2	Hg	1	2
Br	6	4	U	1.5	5

These circumstances, as well as the addition of emissions from heating stoves and boiler houses operating during the cold period of the year, apparently not only suppress purely seasonal effects but also lead to a significant increase in the concentration of rare earth elements (REEs), Cr, Cs, Hg, Na, Sc, and Zn during this period compared to the warm period of the year.

The results of two- and one-factor analyses of variance, where one of the factors is wind direction and the other is wind speed, show that wind

direction and especially wind speed significantly affect the concentrations of most elements in all cities (Table 7).

Table 7.

Degrees of association of element concentrations with wind direction and speed, and their interaction, according to the results of analysis of variance

Element	Wind direction				Wind speed				Interaction		
	S2	N3	N2	V1	S2	N3	N2	B1	N3	N2	B1
Na	3	3	0	4	4	1	3	3	4	0	4
Se	0	0	0	0	0	3	4	4	0	2	0
Cr	4	4	4	4	0	0	4	4	1	2	0
Fe	0	0	0	0	0	4	4	4	0	2	0
Co	0	0	0	0	2	0	3	2	0	0	1
Zn	3	0	2	1	2	4	4	4	3	4	0
Br	0	0	0	4	2	0	0	0	3	0	2
Sb	0	2	0	0	0	0	4	2	0	2	0
Cs	0	0	0	0	0	2	4	3	4	1	0
La	0	0	4	0	0	3	0	4	1	0	0
Sm	0	0	0	0	0	1	4	2	0	1	1
Eu	0	3	0	1	0	2	2	4	3	0	0
Au	3	3	0	0	1	1	3	0	0	3	0
Hg	4	4	0	0	3	0	0	4	0	2	4
Th	2	2	4	0	0	1	4	4	4	1	1
dust	2	0	0	0	3	0	4	4	1	0	0

The interaction factor of wind direction and speed is more significant in Navoi than in Bukhara. The significance of the interaction factor may indicate the presence of two sources of a given element, say, a near source and a relatively distant source, one of which prevails at low wind speeds and the other at high wind speeds. Due to the location of sampling posts near busy roads, the nearest source is transport and local soil, as well as industrial enterprises located within the city itself, while the distant source is industrial enterprises located outside the city. This situation appears to be realized to a greater extent in Navoi. For example, the concentrations of Sb and Hg at low wind speeds and stationary processes are 8.6 ng/m³ and 8.8 ng/m³, while at high speeds they are 11.1 ng/m³ and 11.2 ng/m³, respectively. Such an increase in the concentration of these harmful substances can be associated with their distant sources-chemical enterprises located outside the city. At the same time, in Samarkand, where the main industrial enterprises are located within the city itself, the concentration of a number of elements (Na, Fe, Co, Br, Hg, and Th) increases significantly at low wind speeds and during stationary processes.

Thus, the concentration of most elements in atmospheric aerosols of cities in the Zeravshan Valley is very sensitive to the location and time of sampling, as well as to meteorological parameters. The differences between sampling posts, seasons of the year, as well as prevailing wind directions and speeds, can often be more conveniently established

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using discriminant functions based on a small number of the most characteristic or informative elements.

Within the framework of discriminant analysis, the sample of observations can, in principle, be divided into an arbitrary number of classes. However, in most cases, division into two most important classes is sufficient. In this case, the formulation of the problem is most convenient.

Suppose there are two classes of p-dimensional objects $X(x_1, x_2, \dots, x_p)$ with N_1 and N_2 realizations. From these p-dimensional objects, a one-dimensional variable is constructed that defines the division of observations into classes.

$$D = \sum_i^p c_i \cdot x_i$$

(5)

Where the coefficients c_i are found from the condition of maximizing the function:

$$F = (\bar{D}_1 - \bar{D}_2) / s^2(D)$$

(6)

Here, \bar{D}_1 и \bar{D}_2 - are the mean values of the variable in the first and second classes, respectively, and $s^2(D)$ - is the variance of the variable, estimated by combining data for both classes.

When the coefficients c_i are known, the assignment of a particular observation realization to one of the two classes is carried out by comparing the value of D with a threshold value $D_{\text{threshold}}$. In this case, if $D > D_{\text{threshold}}$, the realization belongs to the first class, if $D < D_{\text{threshold}}$, it belongs to the second class.

Within the framework of linear discriminant analysis, discriminant functions were determined for various factors affecting the concentration of elements in aerosols of the studied cities. The most informative elements sufficient for discriminating different levels of factors always turned out to be only those that differed significantly within the framework of analysis of variance for the corresponding factors (classes) of different cities or for different periods of the year corresponding to different levels of influence of certain factors. This is a very important point from the perspective of implementing discriminant analysis – the most labor-intensive method of statistical processing. Namely, the results of analysis of variance can be used to screen out the most likely elements for inclusion in the discriminant function, which significantly accelerates the process of constructing

such a function. For example, in our case, the computation time was reduced by approximately an order of magnitude compared to the usual method, where all elements without exception were tested for inclusion in the discriminant function. Table 8 presents the coefficients of the discriminant functions obtained by us, along with the justification coefficient of separation (J_{sep}), which shows the proportion (in percent) of observations correctly classified into classes.

Table 8.

Parameters of the discriminant function for separating data classes

City, post	Threshold number	Element (coefficient)	J_{sep} in %
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Classes: two different sampling posts

S2-N3	6.9	Br (-3.3), Sb (-1.7), Co (0.9), Cs (0.25)	87
S2-N2	-4.1	Sm (-3.4), Br (2.2)	75
S2-B1	5.8	Sb (3.2), Br (-2.1), Sm (3.1), Na (-1.8), манн (-1.5)	85
N3-B1	-13.3	Br (4.9), Sb (-1.1), Na (1.7), Sm (-1.6)	96
N2-B1	7.2	Na (-3.1), Sb (2.6)	67
N3-N2	-9.4	Br (3.0), Eu (-0.7), Sm (-1.0)	95

Classes: warm period of the year and cold period of the year

S2	-0.8	Th (2.3)	73
N3	6.5	Th (-1.2), dust (1.7), Na (-2.2), Sb (2.1), Cs (-1.4)	81
N2	3.2	dust (3.6), Sm (-1.9), Hg (-1.1), Cr (-0.5)	82
B1	0.9	Na (-2.8), Br (3.6)	83

Classes: prevailing wind direction and all other wind directions

S2	1.4	Cr (1.8), Na (-3.8), Zn (3.0)	79
N3	4.9	Cr (-1.8), Hg (2.0), Au (0.9), Na (-1.3), Sb (1.3)	84
N2	-1.6	As (2.75)	64
B1	-2	Na (1.7), Br (-2.9), Cr (2.2)	80

Classes: wind speed less than and greater than the annual average

S2	-3.5	Na (4.1), Zn (-3.5)	70
N3	-11.3	Fe (4.9), Na (-2.9)	73
N2	2.0	Th (-3.1), dust (2.9)	88
B1	11.1	Cr (1.2), Hg (-2.1), dust (1.6), La (5.0), Fe (-3.9)	84

Classes: dry soil and wet soil

S2	-0.9	Th (1.9), Eu (0.9), Au (-0.4)	73
N3	1.6	Sc (4.4), Cr (-1.4), Zn (-0.6)	82
N2	1.2	Sm (-2.6), dust (2.6)	73
B1	4.2	Cr (-3.2), Sm (2.4)	65

From Table 8 it can be seen that for Bukhara, the most characteristic element distinguishing this city from others is Na. This is apparently explained by the fact that the soil salinity of Bukhara is higher than the soil salinity of Navoi and Samarkand [10]. Our analyses of the element content in the soils of these cities and adjacent areas also indicate this. A certain contribution to the Na content in the atmosphere of Bukhara can also be assumed from the ecological situation in the Aral Sea region, due to the closer location of Bukhara to the Aral Sea compared to the other two cities and the clear predominance of northern winds in Bukhara.

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As can be seen, wind directions in Bukhara are primarily discriminated by sodium. However, it turned out that the Na content in the atmosphere of Bukhara increases when eastern and southeastern winds prevail. This increase is apparently due to local sources: local soil and construction materials industrial enterprises located in the eastern and southeastern parts of the city. Consequently, the contribution of the Aral Sea, if any, is not yet noticeable against the background of contributions from these sources. However, it can be assumed that the accumulation of salt in the local soil occurred over a fairly long period, including under the influence of the ecological situation in the Aral Sea region, so the role of the Aral Sea cannot be ruled out.

Conclusions.

1. Using statistical processing methods such as regression analysis, analysis of variance (ANOVA), and discriminant analysis, the patterns of spatio-temporal distribution of element concentrations in atmospheric aerosols of large cities in the Zeravshan Valley were studied. In particular, an effective approach for conducting discriminant analysis was proposed, which consists of using the results of analysis of variance for this purpose.
2. Among the cities considered, Samarkand stands out for its relatively high content of almost all studied elements in atmospheric aerosols, which is apparently due to the significant contribution of industrial enterprises, which, unlike in other cities, are mainly located within the city itself;
3. The seasonal variation of element concentrations in Bukhara differs sharply from those in Samarkand and Navoi. This is primarily due to significantly lower amounts of precipitation and higher wind speeds in Bukhara compared to the other two cities, which to some extent suppresses purely seasonal effects in element concentrations in Bukhara. The "activation" of technogenic sources of atmospheric pollution during the cold period of the year, particularly due to seasonal changes in the prevailing wind direction, leads to an increase in element concentrations during this period;
4. The most characteristic element distinguishing the city of Bukhara from others is Na, which is apparently due to the relatively high degree of soil salinity in Bukhara;
5. Atmospheric aerosols in close proximity to roads are sharply distinguished by high contents of Br, Sb, and Hg, which indicates a certain role of transport in this case. However, the main sources of Br, Sb, and Hg are, apparently, still industrial enterprises. The same can be said regarding the origin of Cr;
6. The main sources of Na, Sc, Fe, Th, and rare earth elements (REEs) are road dust and soil. The contribution of industrial enterprises to atmospheric air pollution is most evident in Samarkand. This source of elements also manifests itself in other cities under certain wind directions;
7. Meteorological conditions significantly influence the formation and behavior of the elemental composition of aerosols in the cities of Samarkand, Navoi, and Bukhara. The most characteristic meteorological parameters are: wind speed and direction – for Bukhara; wind direction and air humidity – for Navoi; and air humidity – for Samarkand;
8. Despite the dissimilar behavior of the elemental composition of aerosols in different cities of the Zeravshan Valley, especially depending on meteorological parameters, the cities of Bukhara and Navoi are closer to each other in terms of annual average concentrations of elements.

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