

**TOXIC ELEMENTS IN THE C₁ COAL SEAM OF THE BLAHODATNA MINE OF
PAVLOHRAD-PETROPAVLIVKA GEOLOGICAL AND INDUSTRIAL AREA OF DONBAS**

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**ТОКСИЧНІ ЕЛЕМЕНТИ У ВУГІЛЛІ ПЛАСТА С₁ ШАХТИ «БЛАГОДАТНА»
ПАВЛОГРАДСЬКО-ПЕТРОПАВЛІВСЬКОГО
ГЕОЛОГО-ПРОМИСЛОВОГО РАЙОНУ ДОНБАСУ**

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Abstract. The features of the distribution of toxic elements in the c₁ coal seam of «Blahodatna» mine field are considered. The research aims to establish regularities in the distribution of toxic elements in the coal seam c₁ of Blahodatna mine of Pavlohrad-Petropavlivka geological and industrial area of Donbas.

Samples were taken from mine opening (reservoir samples, selected by the trench method and from duplicates of drill core personally). Content of toxic elements was determined by quantitative emissive spectrum analysis.

The values of the main descriptive statistical indicators were calculated.

With the aim of identify the composition of the geochemical associations, correlation coefficients (r) were calculated between the content of the toxic elements. In a single geochemical association united elements in which the relationship between the content is described by the correlation coefficient that exceeds 0,5, with a significance level of at least 95%.

As a result of the performed studies, maps of the isoconcentrate of toxic elements and maps of the regional constituent of their contents by the area of the mine field were constructed. Linear regression equations are calculated between the concentrations of toxic elements and the main technological parameters of coal.

Analyzing the result of statistical processing of geochemical information and geological and structural characteristics of the coal seam c₁ of «Blahodatna» mine field allowed us to establish, that the formation of the association of cobalt, nickel, vanadium, lead, chrome and manganese is associated with the enrichment of contact zones of the coal seam by these elements and is genetically is due to influence of adsorption and reductive-oxidative barriers on the migration of matter during the diagenesis and catagenesis of coal-bearing series.

The main scientific importance of the results of the performed studies is the establishment of genetic causes that have a significant effect on the distribution of toxic elements in coal seam of c₁.

Keywords: toxic and potentially toxic elements, thickness of a coal seam, ash content, content of total sulfur, map of isoconcentrate, map of the regional constituent of content, linear regression equation.

Introduction. Pavlohrad-Petropavlivka geological and industrial area of Western Donbas administratively belongs to the Pavlohrad district of Dnipropetrovsk region. The study of the features of the distribution of toxic elements in the coal of the seams in this district is associated with increasing requirements for environmental protection, which necessitate the need for new scientifically based methods for predicting the content of toxic elements in rock mass that extracting by mines and mining waste and coal enrichment. For an objective impact assessment of the coal-mining industry and heat power engineering companies on the environmental situation and planning the most effective measures aimed at improving it, it is

necessary to have information about distribution and concentration of toxic elements in coal and host rocks. The special relevance of this problem is determined by the Law of Ukraine «About Subsoil», the decrees of the Cabinet of Ministers of Ukraine No. 22 dated September 30, 1995 and No. 688 dated June 28, 1997, as well as the normative documents of the State Commission for Mineral Reserves [1].

Recent achievements. Previously together with A.I. Chernobuk, D.Ya. Mihalchonok, V.V. Dvoretskyi [2-3] the features of distribution of some toxic elements in products and waste of enrichment of a number of coal preparatory factories in the Donbas were investigated. V.V. Ishkov together with Ye.S. Koziy [4-16] investigated the features of the distribution of some toxic elements in coal seams of the Pavlohrad-Petropavlivka geological and industrial area of Western Donbas, Krasnoarmiisk [17-19] and Donetsk-Makiivka [20-21] geological and industrial areas of the Donbas.

At the same time, wide consideration and analysis of the distribution of toxic elements in coal seam c₁ of «Blahodatna» mine of the Pavlogradsko-Petropavlovskiy geological and industrial area was not performed before.

The research aims to establish regularities in the distribution of toxic elements in the coal seam c₁ of «Blahodatna» mine field.

Method of research. Consideration of the distribution of toxic elements in geological objects of different nature and scale is necessary for the establishment of the laws of their migration, concentration and dispersion. The peculiarity of the performed research was in the impossibility of direct observation of these processes. In this case, consideration of process dynamics is traditionally performed by comparing statistical data and analysis of cartographic materials for the distribution of chemical elements in the objects under consideration. Then the obtained results are interpreted taking into account physico-chemical and geological features. Thus, obtaining information about distribution of chemical elements in geological objects is the first stage of the study, which proceeds from generalization of the actual material, through its theoretical comprehension to verify the revealed regularities by experimental way.

Samples were taken from mine opening (reservoir samples, selected by the trench method [22] and from duplicates of drill core personally by authors with the participation of geological services of coal mining enterprises and industrial exploration organizations in the period from 1981 to 2013. The scope of the control test was 5% of the total volume of samples. All analytical work was carried out in central certified laboratories of production geological exploratory organizations. Content of toxic elements was determined by quantitative emissive spectrum analysis [23]. 6% of duplicate samples are sent to the internal laboratory control. 10% of duplicate samples were subjected to external laboratory control. The tests quality of the results (correctness and reproducibility) was evaluated as the significance of the average systematic error checked by Student's criterion and the significance of the average random error checked by Fisher's criterion. Whereas the aforementioned errors with a significance level of 0,95 are not significant, the quality of the analysis is considered satisfactory.

At the initial stage of the processing of primary geochemical information using Excel 2020 and Statistica 11.0, the values of the main descriptive statistical indicators (selective average arithmetic, its standard error, median, excess, mod, standard deviation, sampling dispersion, minimum and maximum value of content, coefficient of variation, asymmetry of the sample) were calculated, construction of frequency histograms of the contents and the establishment of the law of distribution of toxic elements were carried out.

With the aim of identify the composition of the geochemical associations, correlation coefficients (r) were calculated between the content of the toxic elements. In a single geochemical association united elements in which the relationship between the content is described by the correlation coefficient that exceeds 0,5, with a significance level of at least 95%.

In assessing the relationship of toxic and potentially toxic elements with the organic or mineral part of the coal, the coefficients of affinity with the organic substance F_o were used, which shows the ratio of the content of elements in coal with a low (<1.6) and high density (> 1.7), coefficients of the given concentration F_{HK} , showing the ratio of the content of elements in the fraction i (C_i) to the content of the initial coal, the correlation coefficients of the content of the studied elements and the ash content of coal and the coefficients of given extraction of the element in a fraction of different density.

During the construction of all maps, the Surfer 11 program was used. During the construction of maps, charts and calculation of correlation coefficients, all values of concentrations of TaPTE were normalized by the formula

$$X_{hopm} = (X_i - X_{min}) / (X_{max} - X_{min}),$$

where X_i - is the result of a single determination of the concentration of the element, X_{max} - is the result of the maximum determination of the concentration of the element; X_{min} - is the result of the minimum determination of the concentration of the element;

Rationing was carried out to bring the samples to one scale.

Regularities of changes in cobalt content. The concentration of cobalt varies from 1,61 g/t to 8,59 g/t (Fig. 1a). The average concentration of cobalt in the coal seam is 5,75 g/t. The maximum value is set in the extreme northern part of the plot and timed to the well bore №8469. Concentration of Co does not depend from the depth, content of total sulfur and ash in the coal. The regional component of Co content increases in the southeastern direction. The regional component of the Co content increases in the southeastern direction (Fig. 1b).

A close inverse relationship was established between the content of cobalt and the thickness of the coal seam ($r = -0,89$), a close direct relationship with cumulation of manganese ($r=0,65$), nickel ($r = 0,75$), lead ($r = 0,70$), chrome ($r = 0,77$), vanadium ($r = 0,82$). Linear regression equations

$$Co=1,0503-0,9972 \times m; \quad Co=0,292+0,6676 \times Mn; \quad Co=0,1819+0,761 \times Ni;$$

$$Co=0,153+0,7353 \times Pb; \quad Co=0,2461+0,7082 \times Cr; \quad Co=0,2427+0,6617 \times V.$$

Regularities of changes in manganese content. The content of manganese varies from 109,61 g/t to 226,34 g/t (Fig. 2a).

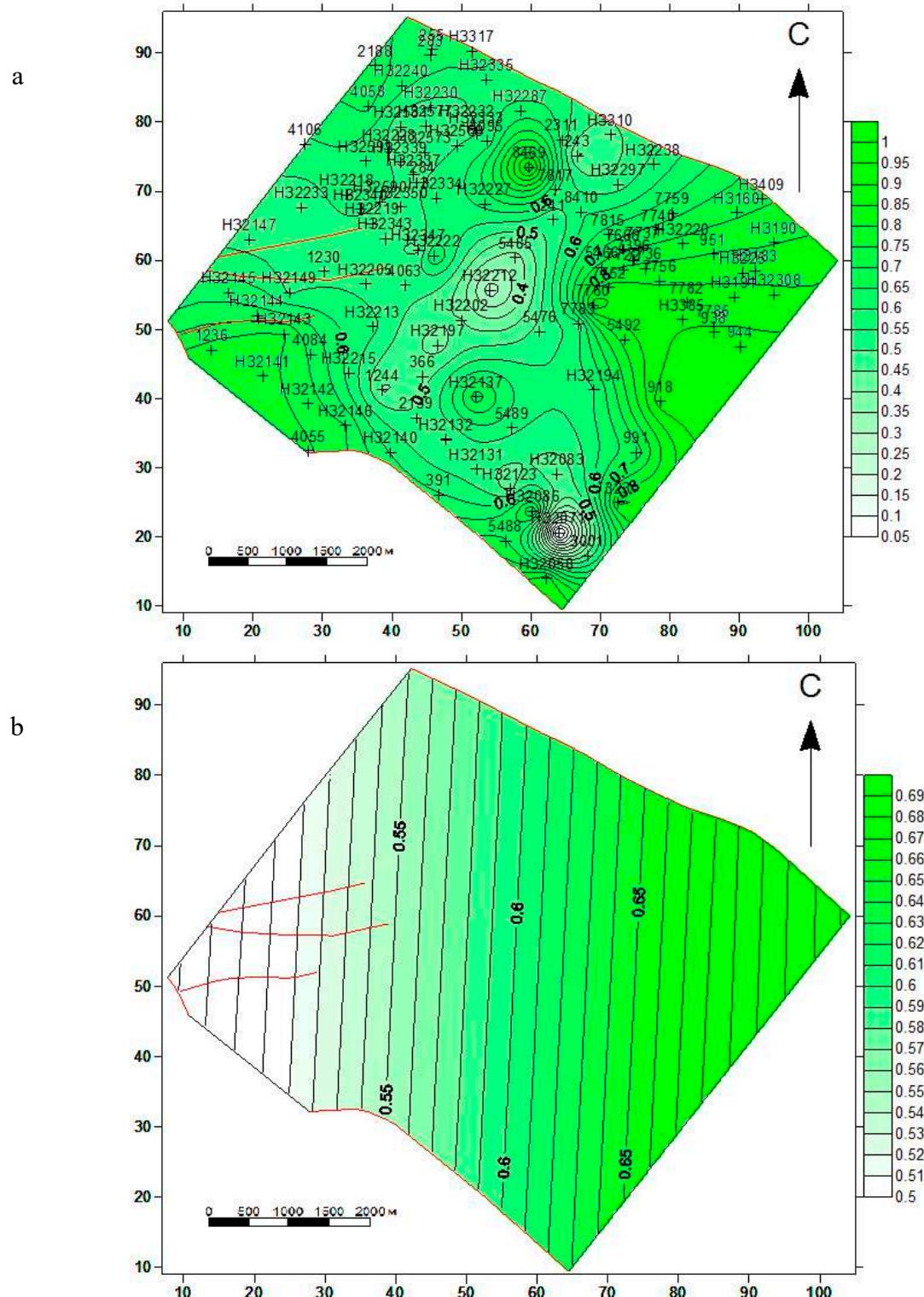


Figure 1: a - Map of isoconcentrate of normalized content of Co in the coal seam c_1 ; b - Map of the regional constituent of normalized contents of Co in coal seam c_1

The average content of Mn in the coal seam is 162,33 g/t. The largest location of manganese is timed to the plot of seam near well bore №7760 in the center of the mine field. Cumulation of Mn does not depend from the depth, content of total sulfur and ash in the coal. The regional component of manganese content increases in the southeastern direction (Fig. 2b).

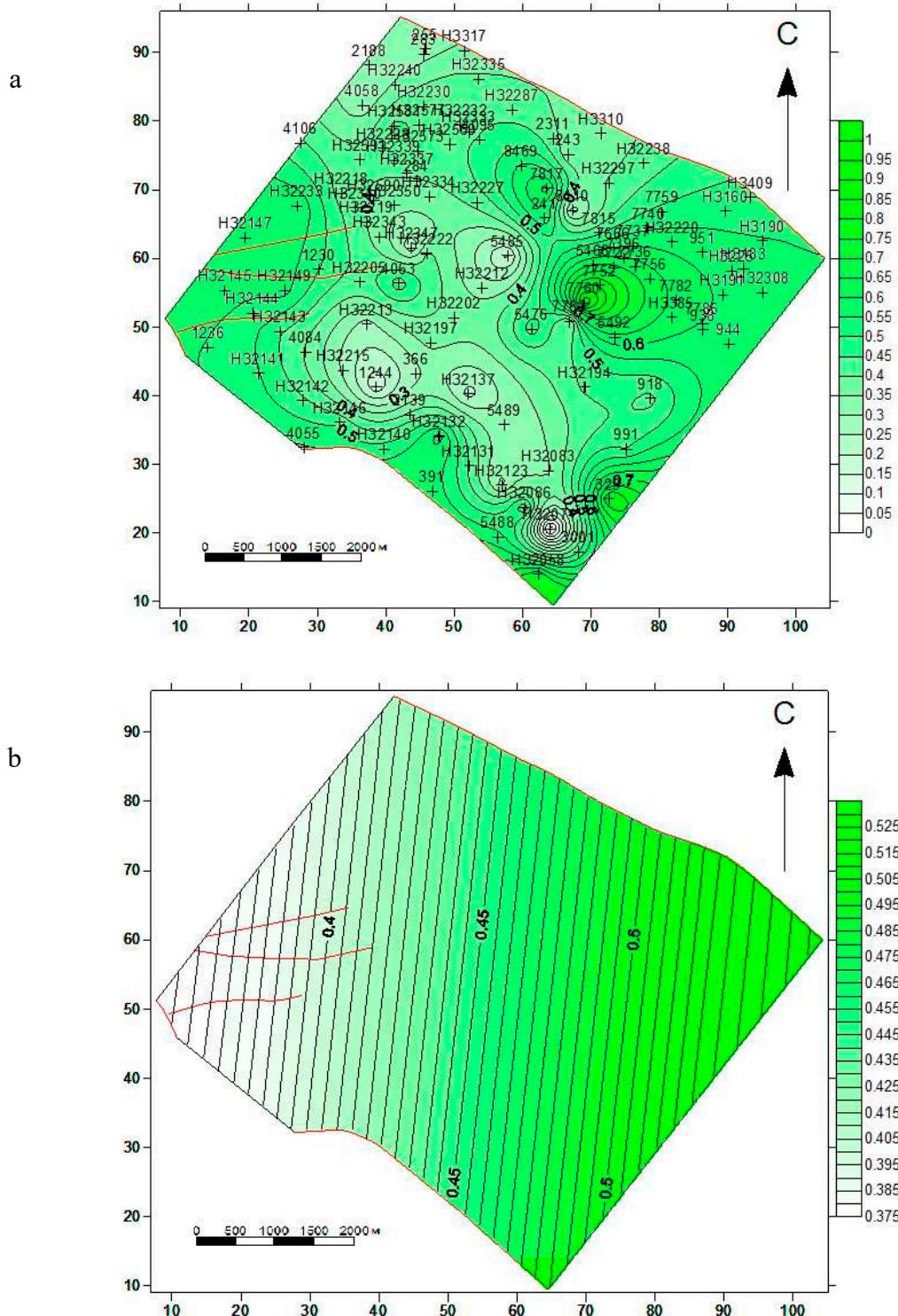


Figure 2: a - Map of isoconcentrate of normalized content of Mn in the coal seam c₁; b - Map of the regional constituent of normalized contents of Mn in coal seam c₁

A close inverse correlation was found between the content of manganese and the thickness of the coal seam ($r = -0,79$), a close direct correlation with the concentration of cobalt ($r = 0,65$), nickel ($r = 0,57$), lead ($r = 0,50$), chrome ($r = 0,67$), vanadium ($r = 0,61$). Linear regression equations

$$Mn = 0,8492 - 0,868 \times m; \quad Mn = 0,0739 + 0,6364 \times Co; \quad Mn = 0,1495 + 0,5586 \times Ni;$$

$$Mn = 0,1691 + 0,4715 \times Pb; \quad Mn = 0,1573 + 0,5999 \times Cr; \quad Mn = 0,1963 + 0,4814 \times V.$$

Regularities of changes in nickel content. Cumulation of nickel ranges from 14,03 g/t to 27,88 g/t (Fig. 3a). The average content of Ni in the coal seam is 21,52 g/t. The plot with largest location of Ni is located in the center of the mine field in the area of the well bore №7760.

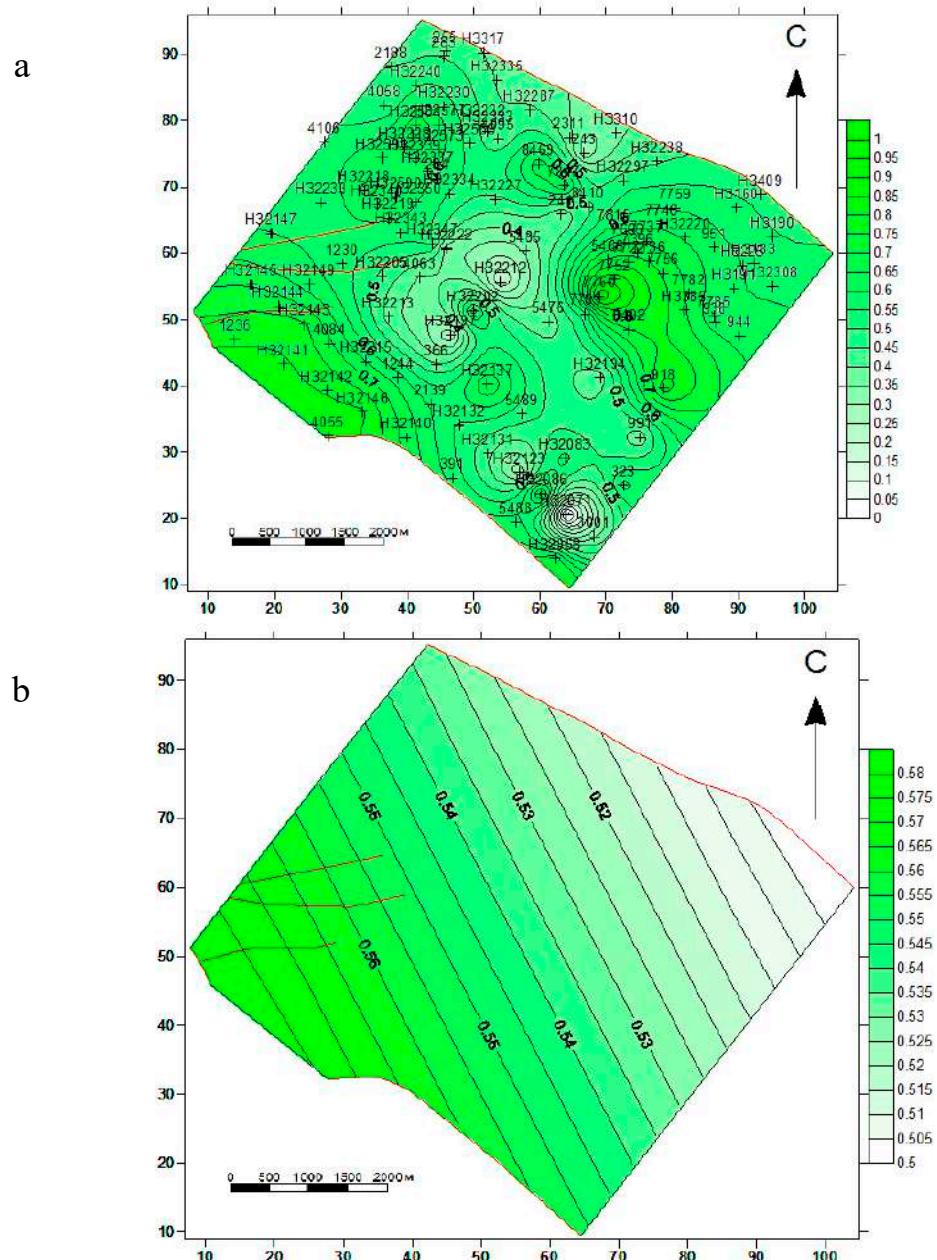


Figure 3: a - Map of isoconcentrate of normalized content of Ni in the coal seam c_1 ; b - Map of the regional constituent of normalized contents of Ni in coal seam c_1

Content of Ni does not depend from the depth, content of total sulfur and ash in the coal. The regional component of nickel content increases in the southwestern direction (Fig. 3b).

Concentration of mercury does not depend from the depth, content of total sulfur and ash in the coal. The regional component of mercury content increases in the northeastern direction (Fig. 3b).

A close inverse relationship was found between the content of nickel and the thickness of the coal seam ($r = -0,81$), a close direct correlation with the concentration of cobalt ($r = 0,75$), manganese ($r = 0,57$), lead ($r = 0,51$), chrome ($r = 0,73$), vanadium ($r = 0,72$). Linear regression equations

$$Ni = 0,9538 - 0,9014 \times m; \quad Ni = 0,0981 + 0,746 \times Co; \quad Ni = 0,2815 + 0,5744 \times Mn;$$

$$Ni = 0,2236 + 0,5296 \times Pb; \quad Ni = 0,216 + 0,6622 \times Cr; \quad Ni = 0,234 + 0,5788 \times V.$$

Regularities of changes in lead content. The content of Pb within the coal seam varies from 4,63 g/t to 14,53 g/t (Fig. 4a). The average content of lead in the coal seam is 10,57 g/t. The largest location is set in the northern part of the mine field near the well bore №8469. Concentration of lead does not depend from the depth, content of total sulfur and ash in the coal. The regional component of lead content increases in the northeastern direction (Fig. 4b).

A close inverse relationship was found between the content of lead and the thickness of the coal seam ($r = -0,72$), a close direct correlation with the concentration of cobalt ($r = 0,70$), manganese ($r = 0,51$), nickel ($r = 0,51$), chrome ($r = 0,63$) and vanadium ($r = 0,66$). Linear regression equations

$$Pb = 0,9543 - 0,7752 \times m; \quad Pb = 0,3945 + 0,4533 \times Mn; \quad Pb = 0,3314 + 0,4951 \times Ni;$$

$$Pb = 0,1992 + 0,6739 \times Co; \quad Pb = 0,3283 + 0,552 \times Cr; \quad Pb = 0,3279 + 0,5115 \times V.$$

Regularities of changes in chrome content. The content of Cr varies in a range from 14,70 g/t to 31,52 g/t (Fig. 5a). The average content in the coal seam is 22,96 g/t. The maximum value is set in the center of the mine field near the well bore №7760. Concentration of chrome does not depend from the depth, content of total sulfur and ash in the coal layer. The regional component of chrome content increases in the southeastern direction (Fig. 5b).

A close inverse relationship was established between the content of chrome and the thickness of the coal seam ($r = -0,86$), a close direct relationship with the cumulation of cobalt ($r = 0,77$), manganese ($r = 0,67$), nickel ($r = 0,73$), lead ($r = 0,63$), vanadium ($r = 0,75$). Linear regression equations

$$Cr = 0,9698 - 1,0458 \times m; \quad Cr = 0,155 + 0,7434 \times Mn; \quad Cr = 0,0591 + 0,798 \times Ni;$$

$$Cr = 0,0644 + 0,7115 \times Pb; \quad Cr = -0,0058 + 0,8365 \times Co; \quad Cr = 0,1423 + 0,6571 \times V.$$

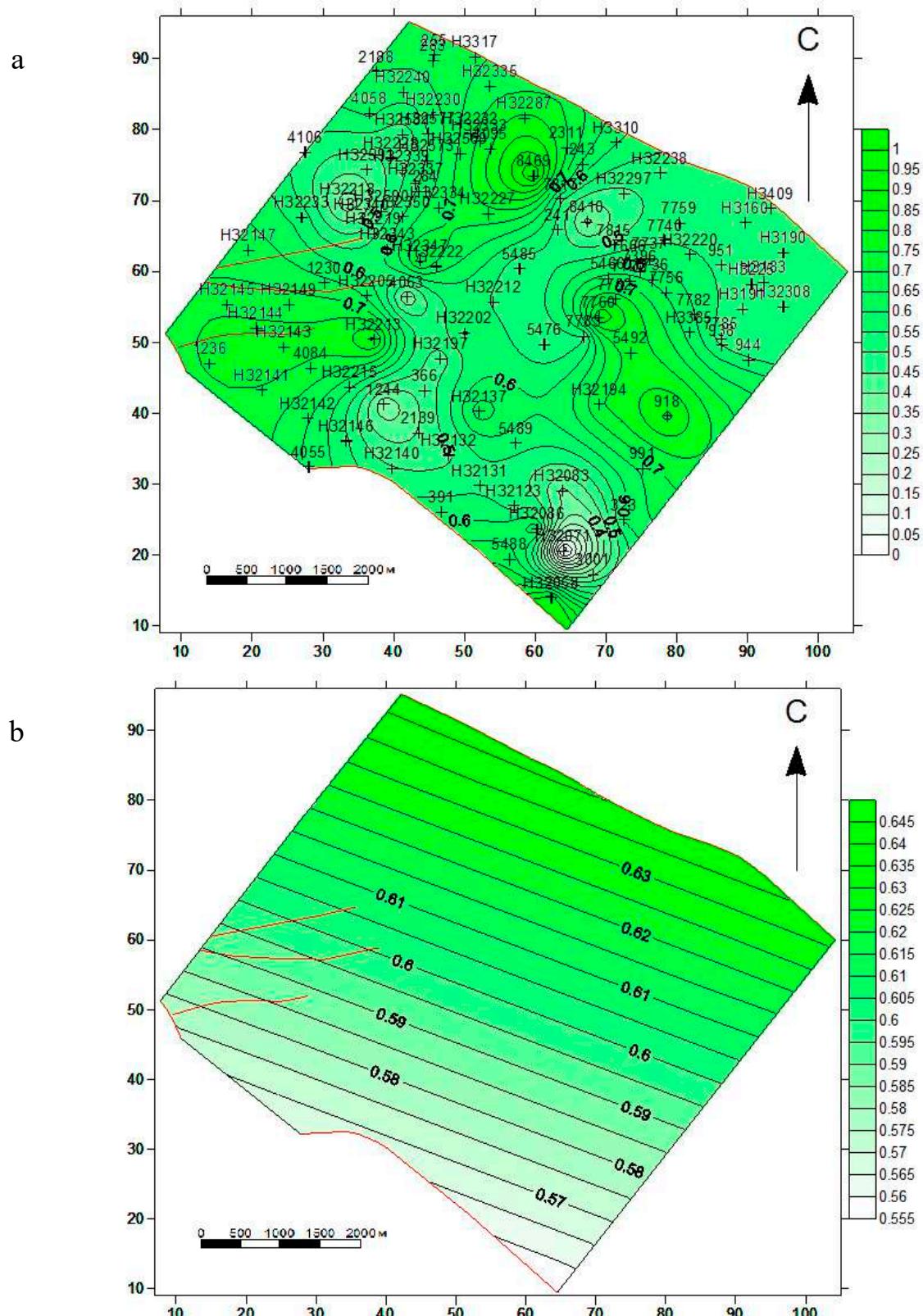


Figure 4: a - Map of isoconcentrate of normalized content of Pb in the coal seam c_1 ; b - Map of the regional constituent of normalized contents of Pb in coal seam c_1

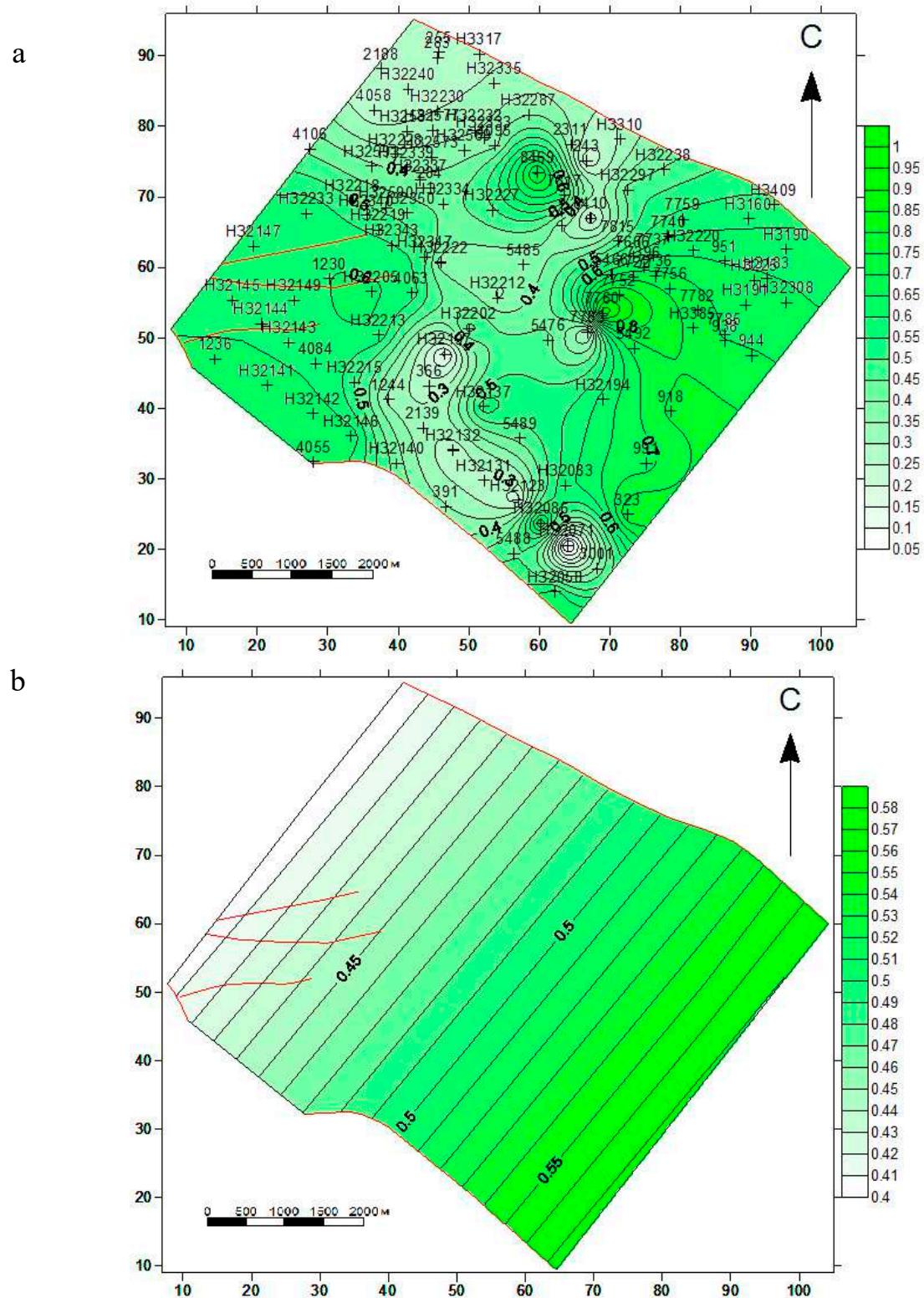


Figure 5: a - Map of isoconcentrate of normalized content of Cr in the coal seam c₁; b - Map of the regional constituent of normalized contents of Cr in coal seam c₁

Regularities of changes in vanadium content. Cumulation of V varies in a range from 17,29 g/t to 35,07 g/t (Fig. 6a). The average content in the coal seam is 26,72 g/t. The maximum value is set in the center of the mine field near the well bore №7760. Concentration of vanadium does not depend from the depth, content of total

sulfur and ash in the coal layer. The regional component of vanadium content increases in the southeastern direction (Fig. 6b).

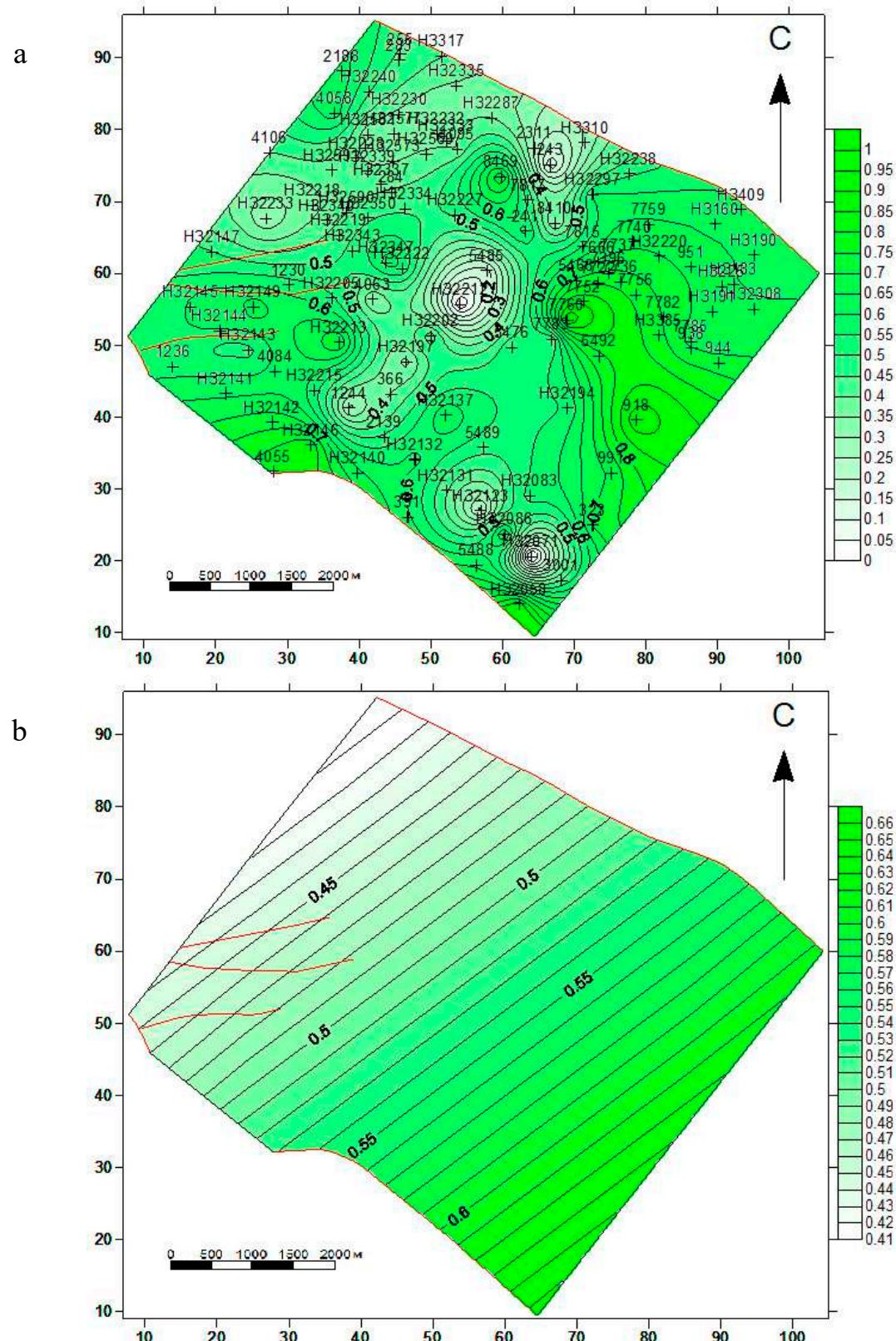


Figure 6: a - Map of isoconcentrate of normalized content of V in the coal seam c₁; b - Map of the regional constituent of normalized contents of V in coal seam c₁

A close inverse relationship was established between the content of vanadium and the thickness of the coal seam ($r = -0,87$), a close direct relationship with the concentration of cobalt ($r = 0,82$), manganese ($r = 0,61$), nickel ($r = 0,72$), lead ($r = 0,66$), chrome ($r = 0,75$). Linear regression equations

$$V=1,0808-1,2017 \times m; \quad V= -0,0718+1,0144 \times Co; \quad V= 0,1806+0,7743 \times Mn;$$

$$V=0,0176+0,8558 \times Pb; \quad V= 0,1118+0,8528 \times Cr; \quad V= 0,0407+0,9052 \times Ni.$$

Conclusions. On the basis of the obtained results of statistical processing of geochemical information and analysis of the maps of isoconcentrate of toxic elements and maps of the regional constituent of their contents, we can do the following conclusions:

- The joint accumulation of such elements as Co, Ni, Pb, Cr, V and Mn, which form the geochemical association and the close negative connection of the concentrations of these elements with the thickness of the coal seam that conditioned of their joint accumulation in the contact areas of the seam with the formation of original zones of enrichment by thickness of 0,15 - 0,2 m.

- The formation of such zones is related with integral effect of the adsorption and oxidation-reducing geochemical barriers in the zone of contact of the coal seam during the migration of the moving forms of the substance of the coal-bearing strata during the process of its diagenesis and catagenesis.

The scientific importance of the obtained results is the determination of the geochemical associations of toxic elements and the genetic causes of their variability in the coal layer, as well as in the detection of polygenic and polychronous nature of their accumulation.

The practical importance of the results obtained is the construction of maps of isoconcentrate toxic elements in the coal seam and the calculation of regression equations between their content and the main technological parameters of coal.

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Анотація. У статті розглянуто особливості розподілу потенційно токсичних елементів у вугіллі пласта с₁ шахти «Благодатна».

Мета роботи - встановити закономірності в розподілі потенційно токсичних елементів у вугіллі пласта с₁ поля шахти «Благодатна» Павлоградсько-Петропавлівського геолого-промислового району Донбасу.

Проби були відіbrane з виробок шахти (колективні проби, відіbrane траншейним методом і особисто з дублікатів керна). Зміст токсичних елементів визначали кількісним спектрально-емісійним аналізом.

Розраховано значення основних описових статистичних показників. З метою виявлення складу геохімічних асоціацій розраховано коефіцієнти кореляції (г) між вмістом токсичних елементів. У єдину геохімічну асоціацію

поєднано елементи, зв'язок між змістом яких описується коефіцієнтом кореляції, що перевищує 0,5, при рівні значимості не нижче 95%.

В результаті виконаних досліджень побудовано карти ізоконцентрат потенційно токсичних елементів і карти регіональної складової їх вмісту по площі шахтного поля. Розраховано лінійні рівняння регресії між концентраціями потенційно токсичних елементів і основними технологічними параметрами вугілля.

Аналізуючи результати статистичної обробки геохімічної інформації по пласту c_1 поля шахти «Благодатна» можна встановити, що формування асоціації кобальту, нікелю, ванадію, свинцю, хрому та марганцю пов'язано із збагаченням цими елементами приконтактових зон вугільного пласта, що можливо генетично обумовлено впливом адсорбційного і окислювально-відновлювального бар'єрів на міграцію речовини у процесі діагенезу і катагенезу угленосної товщі.

Основне наукове значення результатів виконаних досліджень полягає у встановленні генетичних причин, які чинять істотний вплив на особливості розподілу потенційно токсичних елементів у вугіллі пласта c_1 .

Ключові слова: потенційно токсичні елементи, вугільний пласт, карта ізоконцентрат, карти регіональної складової, лінійні рівняння регресії.

Аннотация. В статье рассмотрены особенности распределения потенциально токсичных элементов в угле пласта шахты «Благодатная».

Цель работы – установить закономерности в распределении потенциально токсичных элементов в угле пласта c_1 поля шахты «Благодатная» Павлоградско-Петропавловского геолого-промышленного района Донбасса.

Пробы были отобраны из выработки шахты (коллективные пробы, отобранные траншнейным методом и лично из дубликатов керна). Содержание токсичных элементов определяли количественным спектрально-эмиссионным анализом.

Рассчитаны значения основных описательных статистических показателей. С целью выявления состава геохимических ассоциаций рассчитаны коэффициенты корреляции (r) между содержанием токсичных элементов. В единую геохимическую ассоциацию объединены элементы, связь между содержанием которых описывается коэффициентом корреляции, превышающим 0,5, при уровне значимости не ниже 95%.

В результате выполненных исследований построены карты изоконцентрат потенциально токсичных элементов и карты региональной составляющей их содержания по площині шахтного поля. Рассчитаны линейные уравнения регрессии между концентрациями потенциально токсичных элементов и основными технологическими параметрами угля.

Анализируя результаты статистической обработки геохимической информации по пласту c_1 поля шахты «Благодатная» можно установить, что формирование ассоциации кобальта, никеля, ванадия, свинца, хрома и марганца связано с обогащением этими элементами приконтактных зон угольного пласта, что возможно генетически обусловлено влиянием окислительно-восстановительного барьера на миграцию вещества в процессе диагенеза и катагенеза угленосной толщи.

Основное научное значение результатов выполненных исследований состоит в установлении генетических причин, оказывающих существенное влияние на особенности распределения потенциально токсичных элементов в угле пласта c_1 .

Ключевые слова: потенциально токсичные элементы, угольный пласт, карта изоконцентрат, карты региональной составляющей, линейные уравнения регрессии.

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