East European Journal of Physics. 1. 405-410 (2024)
DOI:10.26565/2312-4334-2024-1-42 ISSN 2312-4334

IDENTIFICATION OF HEAVY METAL POLLUTION SOURCES ON THE TERRITORY ADJACENT TO THE NSC OF "KHARKIV INSTITUTE OF PHYSICS & TECHNOLOGY" BY PMF METHOD

Maryna F. Kozhevnikova*, Volodymyr V. Levenets, Oleksii Yu. Lonin, Oleksandr P. Omelnik, Andriy O. Shchur
NSC "Kharkiv Institute of Physics & Technology" NASU,
1, Academichna str., 61108, Kharkiv, Ukraine
**Corresponding Author e-mail: marko@kipt.kharkov.ua*
Received November 7, 2023; revised January 25, 2024; accepted January 30, 2024

In this paper the content of heavy metals at the territory of Pyatihatki settlement, where the National Scientific Center Kharkiv Institute of Physics & Technology (NSC KIPT) is located. The nuclear-physical methods were used to determine the content of chemical elements in the soil samples taken in 30 points at the territory of Pyatihatki settlement in 2011-2021. The elemental analysis was carried out on the analytical nuclear-physical complex "Sokol". The methods, based on registration of characteristic X-ray radiation of atoms and γ-radiation of nuclei excited by accelerated protons, were used. After the measurements completion, the data arrays on the content of 15 chemical elements (N, Na, S, Cl, K, Ca, Ti, Mn, Fe, Cu, Zn, Zr, Br, Sr, Pb) in the soil samples were obtained. The data arrays processing was carried out using the EPA (Environmental Protection Agency) PMF v3.0.2.2.2 software based on the application of the PMF (Positive matrix factorisation) algorithm. ArcView 3.2a was chosen as the basic software product for the analysis of spatial distribution of the major polluting chemical elements. As a result of the performed work, the pollution sources, which have an impact on the territory near the NSC KIPT, have been identified. The source of the soil pollution is the autostrades, among which the road around the city Kharkiv stands out, where an increase in the content of Pb, Sr, Zr, Cr and Cu was detected. A source of chromium contamination, located presumably to the north-east of Pyatihatki settlement, was identified. The analyses of the obtained data showed that the PMF method allows to identify the factors that affect the soil contamination, and to determine the presumptive sources of pollution with the help of wind rose.
Keywords: *Heavy metals; Elemental analysis; Characteristic X-ray radiation; Positive matrix factorization; Method of principal component analysis (PCA)*
PACS: 89.60.Gg, 89.60-k

INTRODUCTON

A serious environmental problem over the last century has been the intensive development of industry and transport complex, which are the most powerful sources of biosphere pollution. The soil is a poorly migrating medium, which is exposed to heavy metal pollution every day. According to WHO, up to 95% of heavy metals together with the products of plant and animal origin enter the human body through the trophic chains [1].

The soil protection from the pollution is an important problem, since any harmful compounds in the soil, sooner or later, get into the human body. First, there is a constant washing out of contaminants into open water bodies and ground waters, which can be used by people for drinking and other needs. Second, these contaminants from the soil moisture, groundwater and open water bodies get into the organisms of animals and plants that use this water, and then through the food chains again get into the human body. Third, many compounds that are harmful to the human body have the ability to accumulate in tissues, and, above all, in bones [1].

The heavy metals and their compounds form a significant group of toxins, which makes the anthropogenic impact on the ecological structure of the environment and on the humans themselves. First of all, those metals that are most widely and in significant amounts used in human production activities and, as a result of their accumulation in the external environment, pose a serious danger in respect to their biological activity and toxic properties, are of interest. They include Pb, Hg, Cd, Zn, Bi, Co, Ni, Cu, Sn, Sb, V, Mn, Cr, Mo and As.

Table 1 presents the hazard classes of chemical pollutants [2].

Table 1. Hazard classes of chemical pollutants

Class	Elements
1	As, Cd, Hg, Pb, Zn, F, 3,4- benzo(a)pyrene
2	B, Co, Ni, Mo, Cu, Sb, Cr
3	Ba, V, W, Mn, Sr

The soil contamination with heavy metals has different sources: metalworking industry waste; industrial emissions; fuel combustion products; automobile exhaust gases; agricultural chemicals.

Cite as: M.F. Kozhevnikova, V.V. Levenets, O.Yu. Lonin, O.P. Omelnik, A.O. Shchur, East Eur. J. Phys. 1, 405 (2024), https://doi.org/10.26565/2312-4334-2024-1-42

The heavy metal distribution on the soil surface is determined by many factors. It depends on peculiarities of the pollution sources, meteorological features of the region, geochemical factors and landscape conditions in general.

From the historical point of view, an interest in this problem appeared when studying the soil fertility, as long as the elements such as Fe, Mn, Cu, Zn, Mo and Co are very important for the plant life and, consequently, for the animals and humans. They are known as microelements because they are required by plants in small quantities. All the microelements can make a negative effect on the plants if the concentration of their available forms exceeds certain limits. Table 2 presents the data on the effects of heavy metal concentrations on plants [3].

Table 2. Effect of toxic concentrations of some heavy metals on plants

Element	Concentration in soil, mg/kg	Plant response to the increased concentrations of heavy metals
Pb	100-500	Inhibition of respiration and suppression of photosynthesis process; sometimes an increase of cadmium content and a decrease of zinc, calcium, phosphorus, sulphur supply; decrease in the crop yield; deterioration of the plant products quality. External symptoms are the appearance of dark green leaves, curling of old leaves, stunted foliage.
Cd	1-13	Disruption of enzyme activity, processes of transpiration and fixation of CO_2; retardation of photosynthesis, inhibition of biological recovery of NO_2 to NO; difficulty in the supply and metabolism of a number of nutrition elements in plants. External symptoms: growth retardation, root system damage, leaf chlorosis.
Zn	140-250	Chlorosis of young leaves.
Cr	200-500	Deterioration of plant growth and development, wilting of the plant above-ground parts, root system damage, chlorosis of young leaves, sharp decrease in the content of most essential macro- and microelements (K, P, Fe, Mn, Cu, B, etc.) in plants.
Ni	30-100	Suppression of photosynthesis and transpiration processes, appearance of chlorosis signs.

Vehicle gases exhaust, wastewater irrigation, wastes, residues and emissions from the operation of mines and industrial sites, application of phosphorus and organic fertilizers, use of pesticides, etc. have resulted in an increase of heavy metal concentrations in soil.

As long as the heavy metals are firmly bound to the soil constituents and are difficult to access, their negative impact on the soil and environment will be insignificant. However, if the soil conditions allow heavy metals to pass into the soil solution, there is a direct danger of soil contamination, and there is a probability of their penetration into the plants, as well as into the organism of humans and animals that consume these plants. The danger of soil and plant contamination depends on: the type of plants; forms of chemical compounds in the soil; presence of the elements that counteract the influence of heavy metals and substances that form complex compounds with them; the adsorption and desorption processes; the amount of available forms of these metals in soil and the soil-climatic conditions. Thus, the negative influence of heavy metals depends, in essence, on their mobility, i.e. solubility.

The content of Pb in soil usually ranges from 0.1 to 20 mg/kg. Pb from the soils enters plants and accumulates in them. Pb adversely affects the biological activity in soil, inhibiting the enzyme activity by reducing the intensity of carbon dioxide release and the number of microorganisms. Pb also has the ability to be transmitted through food chains, accumulating in plant, animal and human tissues. The lead dust is deposited on the soil surface, adsorbed by organic matter, moves along the profile with the soil solutions, but is carried outside the soil profile in small quantities.

Zn content in soil varies from 10 to 800 mg/kg, but most often it is 30-50 mg/kg. The accumulation of Zn excessive amount negatively affects most of the soil processes: it causes changes in physical and physicochemical properties of soil, reduces its biological activity. Zn suppresses the vital activity of microorganisms, thus disturbing the processes of organic matter formation in soils.

Zn and Cu are less toxic than the above-mentioned heavy metals, but their excessive amount in the metallurgical industry wastes pollutes the soil and inhibits the growth of microorganisms, reduces the enzymatic activity of soils, reduces the plant yield [4].

It should be noted, that the toxicity of heavy metals increases with their combined effect when they act together on the living organisms in the soil. Since the heavy metals are usually found in various combinations both in the fuel combustion products and the metallurgical industry emissions, their effect on the environment surrounding the sources of pollution can be stronger than inferred from the concentration of individual elements.

SUBJECT OF STUDY AND INPUT DATA

The sources of harmful emissions can be located not only in megalopolises, but also in small settlements engaged in knowledge-intensive production, such as Pyatihatki settlement (Fig. 1), where NSC KIPT is located. As a part of the study of the impact of such an enterprise on the environment by nuclear-physical methods, the content of chemical elements in the soil samples, which were taken at 30 points in Pyatihatki in 2011-2021, was determined.

Figure 1. Placement of observation points in the 5-km zone of NSC KIPT

The samples were prepared according to the standard technology. The measurements were performed on the analytical nuclear-physical complex "Sokol" of NSC KIPT [5]. The methods based on the registration of the characteristic X-ray radiation of atoms (it is method 1) and γ-radiation of nuclei excited by accelerated protons (it is method 2) were used. The elements with an order number of 16 and higher were determined by method 1, and the elements with an order number lower than 16 were determined by method 2. The spectra were measured at the proton beam energy of 1.7 MeV, the current of 20...50 nA, and the proton charge on the target of 100...150 μC. The radiation was registered by Si (Li) and Ge (Li) detectors. After the measurements, the data arrays on the elemental content in the soil were obtained. In the range of elements from N to Pb, 15 elements (N, Na, S, Cl, Cl, K, Ca, Ca, Ti, Mn, Fe, Cu, Zn, Zr, Br, Sr, Pb) were selected for further processing.

Using the EPA PMF v3.0.2.2 programme [6], the concentrations of these chemical elements and the calculation errors were investigated.

ArcView 3.2a package was chosen as the basic software product for the spatial distribution analysis of the main polluting chemical elements [7].

ArcView is a geographic information system that is designed to display, edit, spatially analyze, search, and manage geospatial data. This software tool was developed by ESRI (Environmental Systems Research Institute).

The tools of geoprocessing and analysis by ArcView package allow performing complex spatial operations on geographic data such as creating buffer zones around the map objects, clipping, sectioning, merging themes_and data assigning by location.

ANALYSIS METHODS

Many practical methods of environmental monitoring require the use of complex non-trivial computational methods implemented by software. To determine the characteristics and location of the pollution sources, the method, called Receptor Modeling in the scientific literature, has been proposed [8, 9]. Its fundamental principles are the mass conservation and mass balance. The input data are the constituent chemical components contained as elemental concentrations in a large number of samples. The basic mass balance equation for m chemical components in n samples from the contribution from p independent sources can be represented as follows:

$$x_{ij} = \sum_{p} g_{ip} f_{pj} + e_{ij} \ , \tag{1}$$

where x_{ij} is the measured concentration of j-th compound in i-th sample, f_{pj} is the concentration of j-th compound in the material emitted by p-th source (source profile), g_{ip} is the contribution of p-th source to the i-th sample, e_{ij} is the fraction of measurements that cannot be fitted by the model. The decomposition of the x_{ij} matrix in the form (1) represents it by the principal components (PCA - Principal Component Analysis) e.g. g_{ip}, in this case, is the score matrix, f_{pj} is the the loadings matrix, e_{ij} is the matrix of residuals. In general, the task is to determine the number of principal components, which is equal to the rank of the x_{ij} matrix. When the PCA method is used to divide the data into meaningful components, it is often referred to as the factor analysis. The PCA method can be interpreted as projecting the data onto a subspace of lower dimensionality. The resulting residuals of e_{ij} are treated as noise with no meaningful information.

Two computational algorithms UNMIX and PMF have been proposed to determine the composition of sources and the contribution of each of them to the sample with the recorded data [10]. UNMIX is based on eigenvalue analysis. The UNMIX model is a new type of multivariant receptor model based on the PCA method**.** As for the PMF (Positive matrix factorization) algorithm, it differs significantly from other factor analysis methods. All the other methods use singular matrix decomposition. PMF is to use the least squares method to minimize the objective function, which has the form:

$$Q = \sum_{j=1}^{n}\sum_{i=1}^{m}\left(\frac{x_{ij} - \sum_{p=1}^{P} g_{ip} f_{pj}}{s_{ij}}\right)^2, \qquad (2)$$

where s_{ij} is the error estimate of the j-th chemical component measured in the i-th sample. The problem is to minimise the Q function with respect to g_{ip} and f_{pj} subject to the constraints for these variables, which take into account their non-negativity. That is, the source profiles and their contributions to the samples are chosen so as to minimise the sum of all residuals e_{ij}.

To analyse the soil data PMF v3.0.2.2.2 programme was used. Preliminary data, obtained using the programme, can be refined. Two additional algorithms are used for this purpose. The first of them, Bootstrap Runs, randomly selects the non-overlapping blocks of samples, thereby revealing new input data. The second algorithm F_{peak}, uses a rotation transformation for the matrices G and F ($G^* = GT$ and $F^* = FT^{-1}$), so that the contribution of the most significant factors is increased and that of the less significant factors is decreased. It should be noted that the solution of the problem, which is defined by expression (1) is not unambiguous, and the result depends on the qualification and subjective perceptions of the researcher.

RESULTS OF THE RESERCH

An input matrix of 30x10x8 (30 is the number of sampling points, 10 years is sampling period, 8 is the number of chemical elements) was used. The following chemical elements were selected to analyse the pollution source: Ti, Zr, Pb, Mn, Sr, Cu, Cr, Zn. The PMF programme was run with the following parameters: number of iterations – 20; number of factors – 4; starting point for each iteration – 25. As a result of the PMF v3.0.2.2 programme operation, the presumptive sources of pollution were obtained, which are presented in Table 3.

Table 3. Sources of pollution

Factor	Dominant elements	Name
1	Titanium, Zirconium, Plumbum	Ti+Zr+Pb
2	Manganese, Strontium	Mn+Sr
3	Copper	Cu
4	Chromium	Cr

For further operation, the spatial distribution analysis of the main polluting chemical elements at the territory of Pyatihatki settlement was carried out by Arc View software in order to define how the environmental situation has changed judging by the presence of some heavy metals such as Pb, Sr, Cr, Cu and Zr for the period 2011-2021.

When comparing the concentrations of Pb (hazard class 1) in the soil samples during 2011-2021 (Fig. 2), a slight increase in its content near autostrades was detected, which did not exceed the maximum permissible concentration (less than 32 mg/kg) [11, 12].

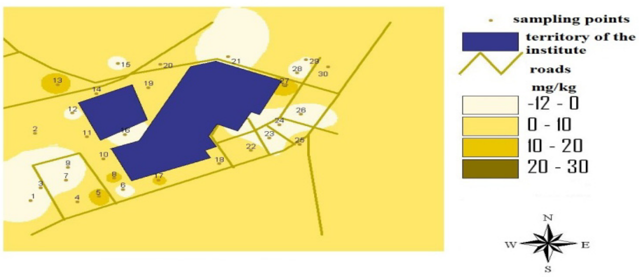

Figure 2. Pb Accumulation 2011-2021 in Pyatihatki settlement

When comparing the concentrations of Sr (hazard class 3) in the soil samples for 2011-2021 (Fig. 3), a slight increase in its content near autostrades, which did not exceed the background concentration (less than 350 mg/kg) was detected.

When studying the accumulation of Cr (hazard class 2) in the soil samples 2011-2021 (Fig. 4), its increase was detected in the eastern part of Pyatihatki settlement. The Cr factor as a source of pollution was detected using the programme PMF v3.0.2.2.2. The 2017 samples were a major contributor to this factor: points 1, 3, 5, 6, 7, 12, 15, 16, 17, 19, 30 showed significant concentrations of chromium, indicating the need for research and action; and points 9 and 20 showing threshold concentrations indicating the need for urgent soil cleanup measures. Such concentrations of chromium in soil cause deterioration of plant growth and development, wilting of the plant above-ground parts, root system damage, chlorosis of young leaves, and a sharp decrease in the content of most essential macro- and microelements (K, P, Fe, Mn, Cu, B, etc.) in plants. When the wind rose was overlaid on the 2017 chromium map, the source of chromium was observed in the north-east direction. In the 2021 samples, the contribution of Cr was insignificant and did not exceed the maximum permissible concentration (less than 100 mg/kg).

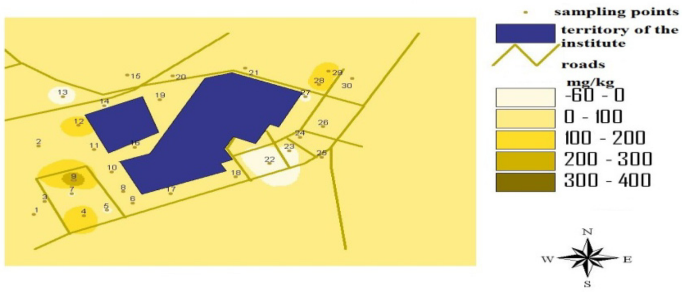

Figure 3. Sr Accumulation 2011-2021 in Pyatihatki settlement

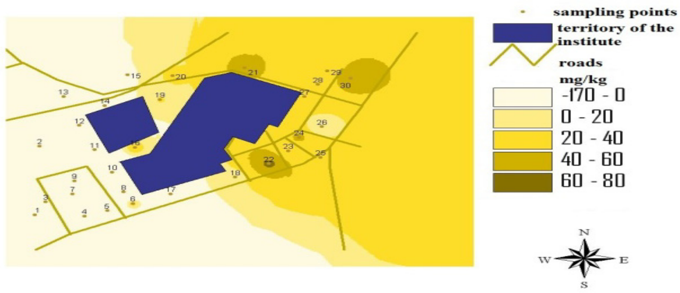

Figure 4. Cr Accumulation 2011-2021 in Pyatihatki settlement

When studying the accumulation of Zr in the 2011-2021 soil samples (Fig. 5), a slight increase in its content near autostrades was detected, which did not exceed the background concentration (200 mg/kg).

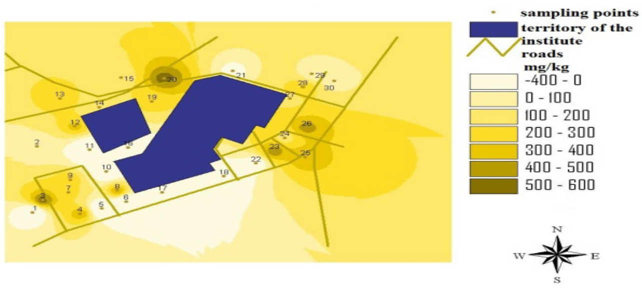

Figure 5. Zr Accumulation 2011-2021 in Pyatihatki settlement

When studying the accumulation of Cu (hazard class 2) in the 2011-2021 soil samples (Fig. 6), a slight increase in its content near autostrades was detected, which did not exceed the maximum permissible concentration (less than 55 mg/kg).

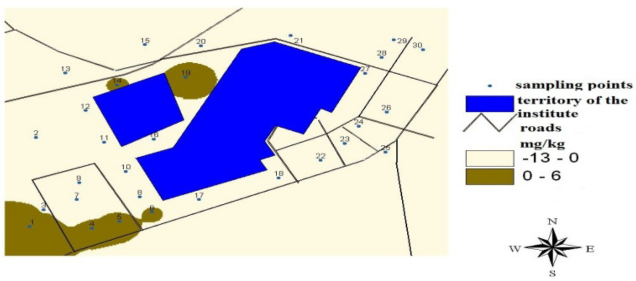

Figure 6. Cu accumulation for 2011-2021

CONCLUSIONS

The nuclear-physical methods were used to determine the content of chemical elements in the soil samples taken in 30 points at the territory of Pyatihatki settlement in 2011-2021. After the measurements completion, the data arrays on the content of elements in the soil were obtained.

For the analysis of the obtained data EPA PMF v3.0.2.2.2 software was used. When studying by PMF method the data on heavy metals concentration in the soil samples for 2011-2021, the sources of pollution, which had an impact on the territory near NSC KIPT, were identified. The sources of the soil pollution are autostrades (especially the road around the city Kharkiv, where an increase in the content of Pb, Sr, Zr, Cr and Cu was identified. A source of chromium contamination, which is located presumably to the north-east of Pyatihatki settlement, has been detected.

Thus, it can be concluded that the PMF method allows to identify the factors that influence soil contamination and to determine the presumptive sources of contamination by the use of the wind rose.

ORCID
Maryna F. Kozhevnikova, https://orcid.org/0000-0003-2464-3847; **Volodymyr V. Levenets,** https://orcid.org/0000-0002-6439-0576
Oleksii Yu. Lonin, https://orcid.org/0000-0002-5386-3825; **Oleksandr P. Omelnik,** https://orcid.org/0000-0003-2467-3632
Andriy O. Shchur, https://orcid.org/0000-0002-6619-4069

REFERENCES

[1] V.P. Seredina, *Загрязнение почв: учебное пособие* [*Soil Pollution: A Study Guide*], (TSU Publishing House, 2015), pp. 346. (in Russian)
[2] I.N. Bezkopylny, "Some methodological approaches to studying the impact of environmental factors on public health in the area of the territorial-industrial complex", Hygienic sanitation, **11**, 24–27 (1984). (in Russian)
[3] B.A. Yagodin, *Агрохимия* [*Agrochemistry*], (Agropromizdat, 1989), pp. 639. (in Russian)
[4] Yu.A. Israel, I.K. Gasilina, and F.Ya. Rovinsky, *Мониторинг загрязнения природной среды* [*Monitoring of environmental pollution*], (Gidrometeoizdat, Leningrad, 1978), pp. 560. (in Russian)
[5] V.N. Bondarenko, L.S. Glazunov, et al., "Analytical installation for nuclear physics analysis methods", Scientific statements. Series: Physics. Belgorod State University, **2(15)**, 86–92 (2001). (in Russian)
[6] *EPA Positive Matrix Factorization (PMF) 3.0 Fundamentals &User Guide*, (U.S. Environmental Protection Agency, 2008), pp. 81. https://nepis.epa.gov/Exe/ZyPDF.cgi/P100GDUM.PDF?Dockey=P100GDUM.PDF
[7] T. Ormsby, *Extending ArcView GIS: with Network Analyst, Spatial Analyst and 3D Analyst*, (ESRI Press, 1999), pp. 527.
[8] P.K. Hopke, "Application of receptor modeling methods", Journal of Chemometrics, **17**, 255–265 (2003). https://doi.org/10.5094/APR.2011.016
[9] M.F. Kozhevnikova, V.V. Levenets, and I.L. Rolik, "The Pollution Source Identification: Computational Approach ", PAST, **6**(76), 149-156 (2011). https://vant.kipt.kharkov.ua/ARTICLE/VANT_2011_6/article_2011_6_149.pdf (in Russian)
[10] E. Kim, T.V. Larson, P.K. Hopke, C. Slaughter, L.E. Sheppard, and C. Claiborn, "Source identification of PM2.5 in an arid Northwest U.S. City by positive matrix factorization", Atmospheric Research, **66**(4), 291–305 (2003). http://dx.doi.org/10.1016/S0169-8095(03)00025-5
[11] *Гігієнічні регламенти допустимого вмісту хімічних речовин у ґрунті. Наказ Міністерства охорони здоров'я України № 1595* [*Hygienic regulations on the permissible content of chemical substances in the soil. Order of the Ministry of Health of Ukraine No. 1595*], (2020). https://zakon.rada.gov.ua/laws/show/z0722-20#Text (in Ukrainian)
[12] S.M. Ryzhuk, M.V.Lisovy, and D.M. Bentsarovsky, *Методика агрохімічної паспортизації земель сільськогосподарського призначення* [*Methodology of agrochemical certification of agricultural lands*], (Kyiv, 2003), pp. 64. (in Ukrainian)

ВИЯВЛЕННЯ ДЖЕРЕЛА ЗАБРУДНЕННЯ ВАЖКИМИ МЕТАЛАМИ НА ТЕРИТОРІЇ, ЩО ПРИЛЯГАЄ ДО ННЦ "ХАРКІВСЬКИЙ ФІЗИКО-ТЕХНІЧНИЙ ІНСТИТУТ", МЕТОДОМ PMF

Марина Ф. Кожевнікова, Володимир В. Левенець, Олексій Ю. Лонін, Олександр П. Омельник, Андрій О. Щур
Національний науковий центр «Харківський фізико-технічний інститут», НАНУ
вул. Академічна, 1, 61108, Харків, Україна

У роботі досліджено вміст важких металів біля пос. П'ятихатки, де знаходиться Національний науковий центр Харківський фізико-технічний інститут (ННЦ ХФТІ). Ядерно-фізичними методами визначено вміст хімічних елементів у пробах ґрунту, які були взяті у 30 точках на території сел. П'ятихатки у 2011-2021рр. Елементний аналіз виконано на аналітичному ядерно-фізичному комплексі «Сокіл». Використані методи, що ґрунтуються на реєстрації характеристичного рентгенівського випромінювання атомів та γ-випромінювання ядер, що збуджуються прискореними протонами. Після проведення вимірювань отримані масиви даних щодо вмісту 15 хімічних елементів (N, Na, S, Cl, K, Ca, Ti, Mn, Fe, Cu, Zn, Zr, Br, Sr, Pb) у пробах ґрунту. Обробка масивів даних проводилася з використанням програми EPA PMF v3.0.2.2, заснованої на застосуванні алгоритму PMF (Positive matrix factorization – позитивне матричне розкладання). Як базовий програмний продукт для просторового аналізу розподілу основних забруднюючих хімічних елементів, вибрано пакет ArcView 3.2a. В результаті виконаної роботи виявлено джерела забруднення, які мають вплив на територію біля ННЦ ХФТІ. Джерелом забруднення ґрунту є автомобільні дороги (особливо окружна дорога міста Харкова), де виявлено збільшення вмісту Pb, Sr, Zr, Cr та Cu. Виявлено джерело забруднення хромом, який розташований приблизно на північний схід від сел. П'ятихатки. Таким чином, можна зробити висновок, що метод PMF дозволяє виявити фактори, що впливають на забруднення ґрунту, та визначити за допомогою троянди вітрів передбачувані джерела забруднення.
Ключові слова: *важкі метали; елементний аналіз; характеристичне рентгенівське випромінювання; позитивне матричне розкладання; метод основних компонентів(PCA)*