Impact of coal mining on heavy metal content in soil and vegetation using XRF analysis

Nadezhda Cash-ool[1], *Urana* Ondar[1*], *Elena* Kashkak[1], *Anay-Kara* Lopsan-Endan[1], and *Aldynai* Khovalyg[1]

[1]Tuvan State University, Department of Chemistry, Kyzyl, Republic of Tyva, 667000, Russia

Abstract. To determine the content of TiO_2, V, Cr, MnO, Fe_2O_3, Ni, Cu, Zn, As, Sr, CaO, Al_2O_3, SiO_2, P_2O_5, K_2O, MgO in soil samples and Zn, Ni, Mn, Ca, Al, K, Mg, P, Sr in plant samples the method of X-ray fluorescence analysis was applied on the territory of the coal mining enterprise, which makes it possible to analyze samples without destroying their basis by chemical and thermal effects. Exceeding the values of the maximum permissible concentrations of certain elements in the studied soil and vegetation samples is mainly noted in samples taken at reference points exposed to technogenic effects. The estimation of the sampling error showed that the coefficient of variation is significant and varies from 7.72 to 27.06% (for soils), from 2.68 to 20.14% (for plants), which once again proves the need to take into account this component of the analysis error, that is, the need to select and analyze parallel samples.

1 Introduction

It is known that with the development of industry and the creation of powerful industrial equipment, the natural environment is increasingly exposed to intense technogenic impact.

In Tuva, the issue of monitoring the state of the environment in the territories of enterprises, in particular the Mezhegey coal deposit, has become urgent.

The main background in the soil cover of the territory of the Mezhegeysky coal deposit is chestnut soils. Alluvial soils are developed along the southern border of the site in the floodplains of the Durgen, Mezhegey, and Teply Klyuch rivers. The dry steppes are dominated by chestnut light loamy and slushy soils.

The field "Mezhegey" is inhabited by species of indigenous plant communities. They are characterized by a high abundance of steppe plant species. The predominant associations are mainly cereals, cereal-wormwood, mixed grass-cereals, floodplain areas are developed in a small steppe. Due to anthropogenic transformation, vegetation degradation is observed in this area as a result of cattle grazing, so the the steppes are at various stages of pasture digression; due to anthropogenic transformation – mainly highways, construction sites and rock dumps.

In the industrial zone there are quarries, coal mines, coal warehouses and administrative and residential complexes, a boiler room, water-reducing wells, spillways of mine and household waters. From the spillways come, Zn, Pb, Co, Ni, Cu, Sr, V. The water at the outlet

[*] Corresponding author: nirs.tgu.tuva@mail.ru

of wastewater treatment plants can be enriched dozens of times with suspended solids, mainly composed of fine coal, some heavy metals – Cu, Cr, Ni.

Rock dumps (heaps of waste) that remain in the developed areas of mines and section during combustion emit pollutant components such as carbon monoxide, sulfur dioxide, nitrogen oxide, hydrogen sulfide, including heavy metals and trace elements, most of which are leached by atmospheric waters and pollute the soil and other environments with toxic elements.

Further, pollutants from the soil through the root system, or during surface dust pollution through the surface of plants, can enter plant organisms, and then into animal tissues along the food chain. The X-ray fluorescence method is one of many multi-element methods that allows analyzing samples without destruction by chemical or thermal action.

In recent decades, X-ray fluorescence analysis, due to its speed and satisfactory accuracy, has been successfully used for chemical analysis of soil [1-4], bottom sediments [5-6] and plant materials [7-14].

Thus, in our work, an assessment of the possibility of X-ray fluorescence Method of biological materials (tissues and organs of pigeons) was studied.

The purpose of this study is X-Ray Fluorescence Method of micro- and macroelements, assessment of heavy metal contamination of soil and vegetation within the Mezhegey coal deposit.

2 Materials and methods

The starting material for the analysis was soil and grass mixture samples taken on the territory of the Mezhegeyugol coal mining enterprise in the Republic of Tyva. The Mezhegey coal deposit is part of the Ulug-Khem coal basin and is located 35-40 km southwest of the city of Kyzyl.

Most of the coals from the Mezhegey deposit belong to grade fatty. In the southern and southeastern parts of the deposit, coals transform into the gas fatty grade. The main use of Mezhege coals is the production of coke.

To study macro- and microelements in soil and vegetation within the study area, a group of samples was taken at reference points. At each reference point, 2 subsamples were selected, which were independently prepared for analysis and analyzed. Sampling points are located near the Durgen, Shangan, Mezhegei, and Elegest rivers, which are part of the Yenisei River basin.

Figure 1 shows the boundary of the license area of the Mezhegeyskoye field and the sampling point.

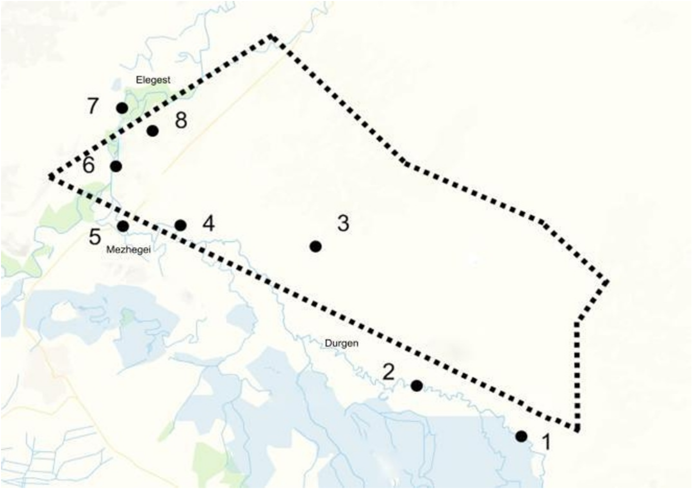

Fig. 1. The boundary of the license area of the Mezhegeysky coal deposit and the reference points of sampling: 1 – Durgen river; 2 – Shangan river; 3 – Mound; 4 – Dewatering well; 5 – Industrial mine water spillway; 6 – Near the bridge over the Mezhegei river; 7 – Industrial waste rock dump (near the Elegest River); 8 – Western flank trunk

The selected soil samples were properly prepared for X-Ray Fluorescence Method: dried at room temperature and crushed in a mechanical grinder to particle sizes <40 μm. This particle size is acceptable when preparing emitters without a binder, and makes it possible to obtain an emitter pellet with a perfectly smooth surface, which is a necessary requirement for X-Ray Fluorescence analysis. Next, emitters in the form of two-layer tablets on a boric acid substrate were prepared from the crushed material.

Similar actions were done for the selected samples of plant cover, with the exception that in this case the samples were ground to a powder state in an agate mortar.

X-Ray Fluorescence intensity measurements were carried out on a spectrometer "SPECTROSCAN MAX" (SPECTRON, Russia), complete with QAV software using a certified standard-background method. The spectroskan is a scanning crystal diffraction vacuum X-ray spectrometer with high reproducibility of measurements at low cost of time per element. In the spectrometric unit, an X-ray tube BHV17 (II) with a lateral X-ray output, with an anode removed, with palladium targets is used as part of the emitter (voltage 60 kV, current strength 4,4 A). K_α - (V, Cr, Mn, Ni, Cu, Zn) and K_β-lines (As) are used as analytical lines. The range of chemical elements to be determined is checked when calculating the counting rates and contrasts on the NaK_α and SrK_α lines.

The standard-background method is based on the fact that using standard samples, the dependences of the ratio of the intensity of the secondary radiation of the element being determined to the intensity of the scattered primary radiation are removed. Then, when analyzing unknown samples, these ratios are compared with the obtained intensity ratios during calibration, the content of the element being determined is found.

To build calibration characteristics and evaluate the accuracy of the determination, analytical signals from calibration soil samples (four sets) were measured: SDPS (saline-podzolic sandy loam soil), SKR (red soils), SSC (gray soils), SChT (typical chernozems) as described in the methodology M-049-P/10 «A method for measuring the mass fraction of metals and metal oxides in powdered soil samples using the X-ray fluorescence method» (in Russian).

The XFA method of plants was graded using standard samples: granulated grass grain flour (TMZg-01), toasted soybean meal (SHSKT), grass mixture (TR-1), Lupine grain (ZL), Canadian elodea (EK-1), soy (C-01), birch leaf (LB-1), Herbal flour of legumes (TMB), Grain of peas (ZG), Compound feed for cattle (KKS), buckwheat groats (KGYA), wheat flour (MP- 01), potato tubers (K- 02), described in the methodology M-049-PM/12 «Method of measuring the mass fraction of Mg, Al, Si, Zn, P, S, Cl, K, Ca, Ba, Ti, Cr, Mn, Fe, Ni, Br, Rb, Sr in powder samples of plant materials by X-ray fluorescence method using X-ray devices for spectral analysis SPECTROSCAN MAX» (in Russian).

The metrological characteristics of the X-ray fluorescence determination of components in soil and vegetation samples by the standard-background method are given in Tables 1 and 2.

Table 1. Metrological characteristics of calibration graphs for determining the mass fraction of components in soil samples

Component	Range of component contents to be determined	LOD
TiO_2, %	0.25-1.60	0.04
Fe_2O_3, %	1.0-8.0	0.2
CaO, %	0.20-12.0	0.10
Al_2O_3, %	3.0-18.0	0.3
SiO_2, %	50-92	1.0
P_2O_5, %	0.035-0.21	0.01
K_2O, %	0.90-2.60	0.06
MgO, %	0.20-3.0	0.07
V, ppm	10-180	7
Cr, ppm	80-180	12
MnO, ppm	100-950	25
Ni, ppm	10-380	15
Cu, ppm	20-310	20
Zn, ppm	10-610	16
As, ppm	20-70	8
Sr, ppm	50-310	20
LOD - limit of detection; confidence probability P=0.95		

Table 2. Metrological characteristics of calibration graphs for determining the mass fraction of components in vegetation samples

Component	Range of component contents to be determined	LOD
Ca, %	0.05-2.8	0.04
Al, %	0.065-0.10	0.003
K, %	0.10-3.5	0.06
Mg, %	0.25-0.45	0.015
P, %	0.10-1.0	0.02
Zn, ppm	15-100	3
Ni, ppm	20-50	1
Mn, ppm	500-1250	15
Sr, ppm	40-1000	10
LOD - limit of detection; confidence probability P=0.95		

3 Results and discussion

In order to assess the environmental situation in the area, study possible sources of emission of heavy metals and main nutrients in the soil and vegetation cover, and the boundaries of the zone of influence of an industrial enterprise, this study presents the results for the last 4 years.

The results of the initial inspection and analysis of the soil structure, physical and general chemical parameters indicate the absence of significant changes in these indicators, which is not surprising for the relatively slow response of ecosystem components to possible changes. The content of basic macroelements and humus in soils and the values of primary production also indicate the above.

The reproducibility of the X-ray fluorescence analysis results in the selected soil and vegetation samples varies depending on the micro- and macro-components to be determined. To assess the contribution of sampling error to the total error, 2 parallel samples were selected and independently analyzed. Table 3 shows the results of assessing the reproducibility of sampling of soil and vegetation cover.

Table 3. Reproducibility of sampling ($S_{r/s}$) of micro and macro elements that are part of soils and vegetation cover

Soil		Vegetation cover	
Indicator	$S_{r/s}$, %	Indicator	$S_{r/s}$, %
V	11.15	Zn	13.07
MnO	17.28	Ni	5.50
Ni	17.08	Mn	9.96
Cu	21.70	Ca	3.12
Zn	16.37	K	3.71
TiO_2	8.47	Al	6.45
Fe_2O_3	10.04	Mg	2.68
CaO	11.83	Sr	3.50
AI_2O_3	7.72		
SiO_2	12.80		
P_2O_5	26.05		
K_2O	16.54		
MgO	27.06		

As the estimation of the sampling error has shown, the value of sampling reproducibility is significant, which proves the need to take into account the sampling error when planning monitoring studies of the state of soils and vegetation cover.

TiO_2, V, Cr, MnO, Fe_2O_3, Ni, Cu, Zn, As, Sr, CaO, Al_2O_3, SiO_2, P_2O_5, K_2O, MgO were determined in the selected soil samples and Zn, Ni, Mn, Ca, Al, K, Mg, P, Sr were determined in plant samples.

As a rule, technogenic halos in soils record the intensity of pollution over the past 20-50 years. The minimum time for the formation of sufficiently contrasting geochemical anomalies in soils depends on the type of exposure and is on average 5-10 years, although for individual elements (As, Zn) it may be 1-2 years. Halos in soil are more static than in air, snow and plants, as soils are able to accumulate pollutants during the entire exposure period.

The content of oxides (%) in soil samples varied in the ranges TiO_2 – 0.34-1.20, CaO – 1.0-11.7, Fe_2O_3 – 2.5-6.4. Al_2O_3 – 4.7-15.1, SiO_2 – 31-68, P_2O_5 – 0.12-0.20, K_2O – 1.36-2.58, MnO – 700-1800, MgO – 1.2-2.5; the content of micro-components (ppm): V – 30-120, Cr – 10-101, Ni – 14-65, Cu – 19-69, Zn – 49-120, As – 2-38, Sr – 110-940.

The results of the analysis of the first group of samples (1 year of study) of soil material from the main reference points show that there is an excess of Zn and As contents in soil samples compared to maximum permissible concentrations (Fig. 2 and Fig. 3). At the Clark level, the contents are marked for Cr, Ni, and Cu.

The content of the main biogenic elements (K, P) mainly in the root horizon of the soil is very low compared to the background values of these elements (potassium from 80 to 500 ppm, phosphorus – from 8.5 ppm to more than 50 ppm). Perhaps this is due to the cessation of the main metabolic processes in plants during the research period.

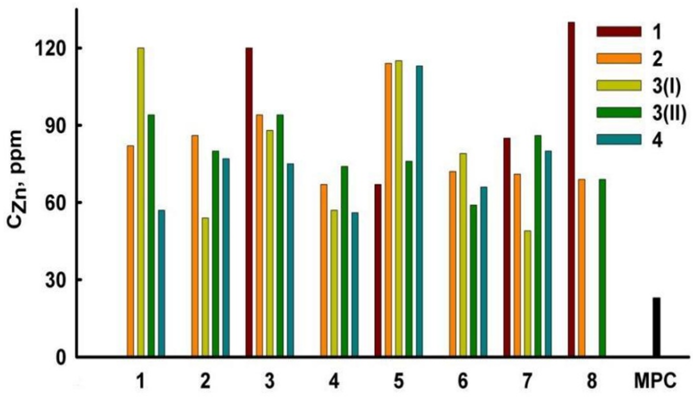

Fig. 2. The dependence of the Zn content in samples taken at reference points on time: 1 – the first year; 2 – the second year; 3 (I) – the first half of the third year; 3 (II) – the second part of the third year; 4 – the fourth year; MPC – the maximum permissible concentration

The content of heavy metals in the soils of reference points characterized as background (reference points 1-3) and subject to technogenic effects (reference points 4-7), as in the previous year, exceed the maximum permissible concentrations for Cr, Ni, Cu, Zn, As, which may indicate their lithogenic origin. It should be noted that the content of the above heavy metals began to exceed regional clarke values, which was not observed in the previous year of observations and can be explained by the already increasing influence of the coal mining enterprise.

If we compare the values of the content in the background areas and in the areas of technogenic impact, there are reliably distinguishable high values of heavy metals in the latter, which indicates the presence of a technogenic source of migration of the substance.

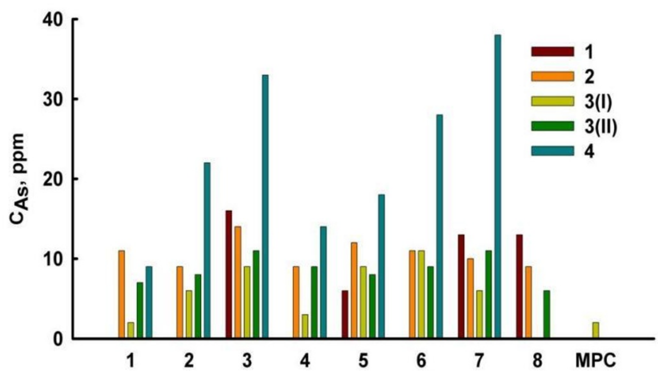

Fig. 3. The dependence of the As content in samples taken at reference points on time: 1 – the first year; 2 – the second year; 3 (I) – the first half of the third year; 3 (II) – the second part of the third year; 4 – the fourth year; MPC – the maximum permissible concentration

If we trace the content of elements by years, it can be noted that in comparison with the first year of the study, in 2-4 years the content of heavy metals in the soils of reference points characterized as background (reference points 1-3) and subject to technogenic effects (reference points 4-8) exceed the maximum permissible concentrations for Cr, MnO, Ni, Cu, Zn, As, which may indicate their lithogenic origin. It should be noted that exceeding the regional clarke values of the content of the above heavy metals at points 1, 3, 6, 7 began to be observed from the second year of the study and this can be explained by the climatic conditions of the year. The increased content of arsenic is probably due to the fact that there is a deposit of arsenide cobalt-nickel ores not far from the coal mining enterprise.

Comparison of the content of chemical elements in the background areas and in the areas of technogenic impact showed that the differences are unreliable and are within the limits of statistical errors, which indicates the subordinate role of technogenic soil pollution in the research area.

The content of most chemical elements in plants of background and potentially polluted territories is below the maximum permissible concentrations and world clarkes for terrestrial vegetation, with the exception of Ni content indicators (Fig. 4).

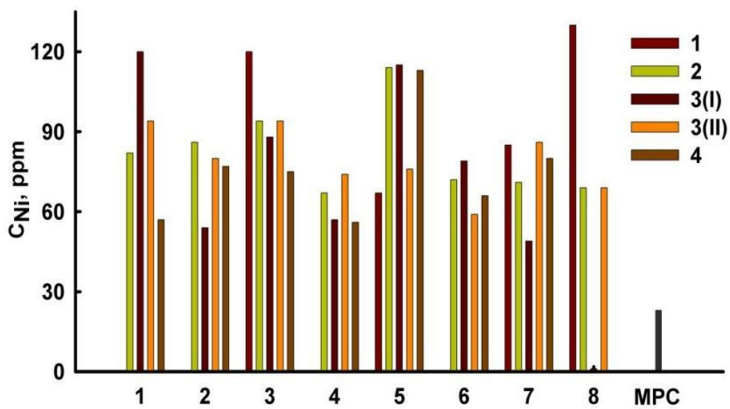

Fig. 4 The dependence of the Ni content in samples taken at reference points on time: 1 – the first year; 2 – the second year; 3 (I) – the first half of the third year; 3 (II) – the second part of the third year; 4 – the fourth year; MPC – the maximum permissible concentration

The content of elements (%) in the samples of vegetation cover varied in the ranges: Ca – 0.24-2.70, Al – 0.07-1.00, K – 0.23-3.50, Mg – 0.13-0.43, P – 0.02-0.45; the content of micro-components (ppm): Zn – 9-53, Ni – 0.8-7.0, Mn – 23-700, Sr – 14-360.

Perhaps this is due to a decrease in the intensity of biological absorption of elements in arid regions in general and the time of sampling for chemical analysis. The accumulation of these elements in plants is determined primarily by the microelement composition of soils associated with soil-forming rocks. This is evidenced by uniform indicators of the microelement composition of soils from background and potentially contaminated areas. In the zone of technogenic pollution by the wind rose, polyelementality is noted in the landscape components. At the same time, complexes in the surface horizons of soils and vegetative organs of herbaceous plants indicate common sources and similarity of the behavior of heavy metals in various landscape-geochemical conditions.

The number of organo-mineral compounds in the surface horizons of the soil has a decisive influence on the accumulation of all the elements under consideration, since many organo-mineral compounds are weakly mobile, and with increased humification, the adsorption strength on the biogeochemical barrier increases.

The content of most heavy metals in plants of background and potentially polluted territories is below the maximum permissible concentrations and global clarke, with the inclusion of Zn and Ni content indicators. Compared to last year, there is a significant decrease in the content of these elements (1-2 times). It should be noted that such a picture in plants may be associated with a decrease in the intensity of biological absorption in a dry year.

The results of the analysis of vegetation samples at the reference points clearly indicate the absence of accumulation of toxic pollutants in the vegetation and their average values are below acceptable values, their content remained at the level of the first year of research and there is no tendency to accumulate them in various aboveground plant organs of the research area.

Figure 5 shows that there is a significant increase in the Zn content in the samples over time, starting from the first year of the study, which can be explained by the influence of a coal mining enterprise. The samples were taken near industrial effluents of mine waters (reference point No. 5). In other samples, this pattern is not observed. For the remaining heavy metals in all analyzed samples, there is no clear dynamics of changes in their contents over time.

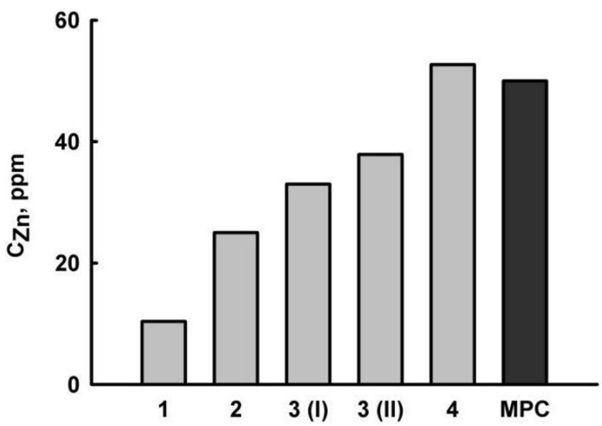

Fig. 5 Dependence of the Zn content in samples taken at reference point No. 5 (industrial mine water spillway) from time to time: 1– the first year; 2 – the second year; 3 (I) – the first part of the third year; 3 (II) – the second part of the third year; 4 – the fourth year; MPC – maximum permissible concentration

The value of the Fe/Mn ratio in the aboveground organs of plants in the studied zones indicates a significant imbalance in the ratio of elements (13.6).

4 Conclusions

Monitoring studies of the state of soils and vegetation cover in the area of influence of the coal mining enterprise were carried out using the X-ray fluorescence analysis method. The X-ray fluorescence methods of soil and plant analysis were graded using standard composition samples.

The technique of X-ray fluorescence analysis makes it possible to analyze micro- and macro-components in prepared powdered soil and vegetation samples without destroying their foundations. The accuracy of the analysis lies within the acceptable values according to our methodology.

The possibility of multi-element analysis, low time costs (the duration of a complete analysis of 6 samples does not exceed 3 hours), relatively simple, rapid and economical sample preparation make X-ray fluorescence analysis quite competitive.

The estimation of the sampling error showed that the coefficient of variation characterizing the sampling error is significant, which once again proves the need to take into account this component of the analysis error, that is, the need for the selection and analysis of parallel samples in environmental studies. Assessment of heavy metal contamination of soils and plants showed some excess of their contents, especially in samples taken near the discharge of mine waters. A significant increase in the content of some heavy metals in soils is of some concern. Against the general background, the content increases at all reference points associated with the technological site do not show significantly high values of their content, and the variations are within the limits of statistical errors. The excess of the maximum permissible concentration values of some elements in the studied samples of vegetation cover is mainly noted in samples taken at reference points exposed to technogenic effects.

Acknowledgments

Prepared with the financial support of the Russian Science Foundation as part of the scientific project "Study of patterns of carbon stock formation in biological systems and landscapes in the transition space from North Asia to Central Asia" **(Grant No. 23-14-20015)**. Scientific project **Grant No. 23-14- 20015** of the Russian Science Foundation.

References

1. R. Ravansari, S.C. Wilson, M. Tighe, Portable X-ray fluorescence for environmental assessment of soils: Not just a point and shoot method. Environment International. **134**, 105250 (2020) https://doi.org/10.1016/j.envint.2019.105250
2. S. Xue, et al., Spatial distribution, environmental risks, and sources of potentially toxic elements in soils from a typical abandoned antimony smelting site. Journal of Environmental Sciences. **127**, 780–790 (2023) https://doi.org/10.1016/j.jes.2022.07.009
3. A. Rawal, et al., Determination of base saturation percentage in agricultural soils via portable X-ray fluorescence spectrometer. Geoderma. **338**, 375–382 (2019) https://doi.org/10.1016/j.geoderma.2018.12.032
4. S. Kabiri, N.M. Holden, R.P. Flood, J.N. Turner, S.M. O'Rourke, X-ray Fluorescence Core Scanning for High-Resolution Geochemical Characterisation of Soils. Soil Systems. **8,** 2 56 (2024) https://doi.org/10.3390/soilsystems8020056
5. A.A. Amosova, V.M. Chubarov, G.V. Pashkova, et al., Wavelength dispersive X-ray fluorescence determination of major oxides in bottom and peat sediments for paleoclimatic studies. Applied Radiation and Isotopes. **144**, 118–123 (2019) https://doi.org/10.1016/j.apradiso.2018.11.004
6. A. L. Finkelshtein, R. V. Smely, A. A. Amosova, V. M. Chubarov, Estimation of the Biogenic Silica Content in Lacustrine Bottom Silicate Sediments by X-Ray Diffraction (XRD) and X-Ray Fluorescence (XRF). Analytical Letters. **55,** 7 1119–1130 (2021) https://doi.org/10.1080/00032719.2021.1988632
7. G. A. Capobianco, et al., A Green Approach Based on Micro-X-ray Fluorescence for Arsenic, Micro- and Macronutrients Detection in Pteris vittata. Water. **14,** 14 2202 (2022) doi: https://doi.org/10.3390/w14142202

8. O.A. Belykh, E.V. Chuparina, Study of the chemical composition of aboveground lingonberries. Proceedings of Universities. Applied Chemistry and Biotechnology. **9.1,** 28 (2018) https://doi.org/10.21285/2227-2925-2019-9-1-118-124
9. I. Allegretta, et al., Rapid multi-element characterization of microgreens via total-reflection X-ray fluorescence (TXRF) spectrometry. Food Chem. **296,** 86–93 (2019) https://doi.org/10.1016/j.foodchem.2019.05.187
10. S. Zhou, et al., Elemental assessment of vegetation via portable X-ray fluorescence: Sample preparation and methodological considerations. Spectrochim Spectrochimica Acta Part B: Atomic Spectroscopy. **174,** 105999 (2020) https://doi.org/10.1016/j.sab.2020.105999
11. M.P. Makarova, A. V. Syroeshkin, T. V. Maksimova, et al., Features of Microelements Express-determination in Medicinal and Nonoficinal Plants by X-Ray-Fluorescence Analysis. Drug development & registration. **8,** 2 93–97 (2019) https://doi.org/10.33380/2305-2066-2019-8-2-93-97
12. N.A.C. Mendes, et al., Selenium Increases Ureide Metabolism and Yield of Cowpea Plants: Examining Se Distribution in Leaves and Seeds Using Microprobe X-Ray Fluorescence Spectroscopy. Gesunde Pflanzen. **75,** 5 (2023) https://doi.org/10.1007/s10343-023-00840-5
13. A. Van der Ent, et.al., Herbarium X-ray fluorescence screening for nickel, cobalt and manganese hyperaccumulator plants in the flora of Sabah (Malaysia, Borneo Island). Journal of Geochemical Exploration. **202,** 49–58 (2019) https://doi.org/10.1016/j.gexplo.2019.03.013
14. E.M. Lyakh, E.P. Khramova, A.Y. Lugovskaya, et al., Synchrotron Radiation X-Ray Fluorescence Analysis in Studying Siberian Shrubs of an Urban Ecosystem. Bulletin of the Russian Academy of Sciences: Physics, **87,** 643–648 (2023) https://doi.org/10.3103/S1062873822701738