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ASSESSMENT OF TOXIC ELEMENTS IN ATMOSPHERIC DEPOSITION IN AZERBAIJAN USING MOSS BIOMONITORING METHODS

Abstract: This study investigated atmospheric heavy metal deposition across three western regions of Azerbaijan - Goygol, Gadabay, and Dashkasan - within the framework of the UNECE International Cooperative Programme on Effects of Air Pollution on Natural Vegetation and Crops (ICP Vegetation), employing moss biomonitoring as the primary investigative approach. Two dominant moss species, *Hylocomium splendens* and *Pleurozium schreberi*, were collected and analysed for a total of 44 elements using a combination of neutron activation analysis (NAA), atomic absorption spectroscopy (AAS), and particle-induced X-ray emission (PIXE). Interelemental relationships were examined through factor analysis, which yielded four distinct factors representing major source groups. When Azerbaijani moss data were compared against Norwegian reference values, elevated concentrations of most heavy metals - including Mg, Al, V, Fe, As, Mo, Cd, La, and U - were recorded in the sampled material. Mosses were utilised as passive bioindicators to quantify elemental pollutant loads in atmospheric deposits and characterise the general pollution status of each study area. Geospatial distribution maps were generated to delineate the most heavily polluted zones and establish links to known contamination sources. Elemental concentrations in mosses collected from Dashkasan and Gadabay were found to substantially exceed those measured in Goygol samples, reflecting the stronger anthropogenic influence in the former regions. In addition to industrial and agricultural pressures, local geological characteristics - specifically lithology and soil composition - were identified as contributing factors governing spatial variability in elemental distribution.

Keywords: air pollution, moss biomonitoring, neutron activation analysis, atomic absorption spectroscopy, particle-induced X-ray emission

Introduction

Over recent decades, plant-based biomonitoring approaches - encompassing mosses, lichens, algae, and tree foliage - have emerged as reliable tools for investigating atmospheric contamination by heavy metals and other biologically harmful substances. Among these, moss-based biomonitoring stands out for its simplicity, cost-effectiveness, and practical applicability. The approach relies on systematic collection and comparison of

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moss samples across a study region, enabling detection of spatiotemporal shifts in air pollution levels and identification of heavily affected zones [1-5].

Data accumulated through moss biomonitoring programmes constitute a critical knowledge base for international policy discussions on transboundary heavy metal pollution. Such studies make it possible to trace both spatial gradients and long-term temporal dynamics of metal deposition in atmospheric particulates, as well as to pinpoint areas exposed to both long-range transported pollutants and locally emitted contaminants. Mosses are particularly suited to this purpose because they passively accumulate heavy metals and trace elements directly from precipitation and the atmosphere, displaying remarkable tolerance even under high contamination levels. The species most frequently employed in sediment biomonitoring programmes are *Hylocomium splendens*, *Pleurozium schreberi*, and *Hypnum cupressiforme*, which have been extensively utilised in tandem with nuclear analytical techniques to map heavy metal deposition patterns across Western Europe [6-8].

Heavy metal contamination of the atmosphere represents a serious threat to both ecological integrity and human wellbeing. Consequently, passive biological monitoring techniques - particularly those utilising mosses - have attracted growing scientific interest as practical means of quantifying atmospheric metal deposition. A key advantage of mosses over vascular plants is their exclusive reliance on aerial nutrient and pollutant inputs, as they lack a root system that could introduce soil-derived interference, making them highly accurate recorders of airborne deposition [9-14].

Uptake of elements by mosses occurs predominantly through wet and dry atmospheric deposition and gaseous absorption, rendering them highly sensitive indicators of ambient air quality - particularly in woodland settings where these species flourish. *Hylocomium splendens*, *Pleurozium schreberi*, and *Hypnum cupressiforme* are the most widely adopted species within standardised European monitoring frameworks, underpinning multi-decade continental surveillance efforts [15-17].

The proven capacity of mosses to reflect both spatial distribution and temporal evolution of heavy metal deposition has made them indispensable in environmental risk assessment, enabling the tracing of pollution to either diffuse long-range transport or concentrated point sources. These scientific needs have driven the establishment of coordinated monitoring initiatives at national and supranational levels. A flagship example is the ICP Vegetation programme, operating under the auspices of the United Nations Economic Commission for Europe (UNECE), which conducts continent-wide sampling every five years and compiles standardised deposition maps [18, 19].

Within Azerbaijan, the western regions of Goygol, Gadabay, and Dashkasan warrant particular attention from an atmospheric monitoring perspective, given their long history of intensive industrial exploitation and agricultural land use. The cumulative anthropogenic burden on these ecologically sensitive territories has generated documented environmental degradation, making the deployment of standardised biomonitoring methodologies both timely and scientifically necessary for informed pollution management [20-24].

The main goal of the research was to determine atmospheric deposition of heavy metals in the study areas and to identify the sources of pollution using moss biomonitoring techniques.

Considering the current state of knowledge on this issue, the aims and objectives of the study required the formulation and solution of the following tasks:

- To develop a biomonitoring network for determining heavy metals and other elements in atmospheric deposition across Goygol and neighbouring regions, including Dashkasan and Gadabay;
- To perform multi-element analysis of moss samples collected from the study area using neutron activation analysis (NAA), particle-induced X-ray emission (PIXE), and atomic absorption spectroscopy (AAS);
- To determine the local background concentrations of elements for the studied territories;
- To prepare pollution maps of the studied areas in order to identify locally emitted pollutants and assess their impact on adjacent regions;
- To use multivariate statistical methods to identify the main sources (factors) of elemental accumulation in mosses and to estimate the contribution of each factor to the overall elemental composition;
- To determine the spatial distribution patterns of heavy metals and other pollutants in atmospheric deposition;
- To assess the integrated pollution level of the study area;
- To justify strategies for reducing anthropogenic (technogenic) impacts on the environment.

Materials and methods

Study areas

The study areas include Goygol and neighboring Dashkasan and Gadabay regions of the western part of Azerbaijan (Fig. 1).

Climatic indicators in the Goygol region vary according to altitude. In the foothills and low mountains, the climate is mild-warm with dry winters, in the middle highlands, cold and dry winters, and in the highlands, the mountain tundra climate prevails.

The main economic activities of the region are grain growing, potato growing, cattle breeding, sheep breeding, fruit growing, vegetable growing, beekeeping, poultry farming and grape growing. Viticulture and animal husbandry occupy an important place in the economy of the region. There is a mining industry, gravel factories, manufacturing and household service complexes, a winery and other industrial enterprises [25-27].

The surface of Dashkasan, located in the northeast of the Lesser Caucasus, is surrounded by mountains from the north. The slopes of the Murovdag and Shahdag ridges are also part of this region. The highest peaks are Hinaldag (3367 m), Goshgar mountain (3361 m), etc.

Dashkasan district is one of the important mining ore industry districts of the republic. The main part of the region's industry is the metallurgical industry. Minerals are iron ore, cobalt, alunite, marble, limestone, etc. Currently, reserves of 3 iron ore deposits have been confirmed in the country. These are "Dashkasan", "Janubi Dashkasan" and "Demir" mines located in the Dashkasan district. "Dashkasan Ore Dressing" OJSC is the exclusive user of iron ore deposits in the Dashkasan region, the owner of the ore extraction and ore refining plant and equipment. The district is also an agricultural district. Agricultural activity is mainly animal husbandry, crop cultivation, beekeeping and poultry farming. Large-horned cattle and small-horned animals are kept in the livestock area [28-30].

The Gadabay region is located in the middle and high mountain belt of the Lesser Caucasus. The territory of the district covers the northern slope of the Shahdag ridge, a part of the Bashkend-Dastafur depression and the Shamkir mountain massif.

The economy mainly consists of agriculture. Potato farming, animal husbandry and grain farming are dominant in its economy. There is Gadabay copper smelting plant (1855-1956) and Galakand copper smelting plant (1883) created on the basis of copper ore discovered (1849) in the region [31, 32].

Atmospheric air pollution is attributed to any property or composition change that has a negative impact on human health, the state of vegetation, the animal world, and the ecosystem in general.

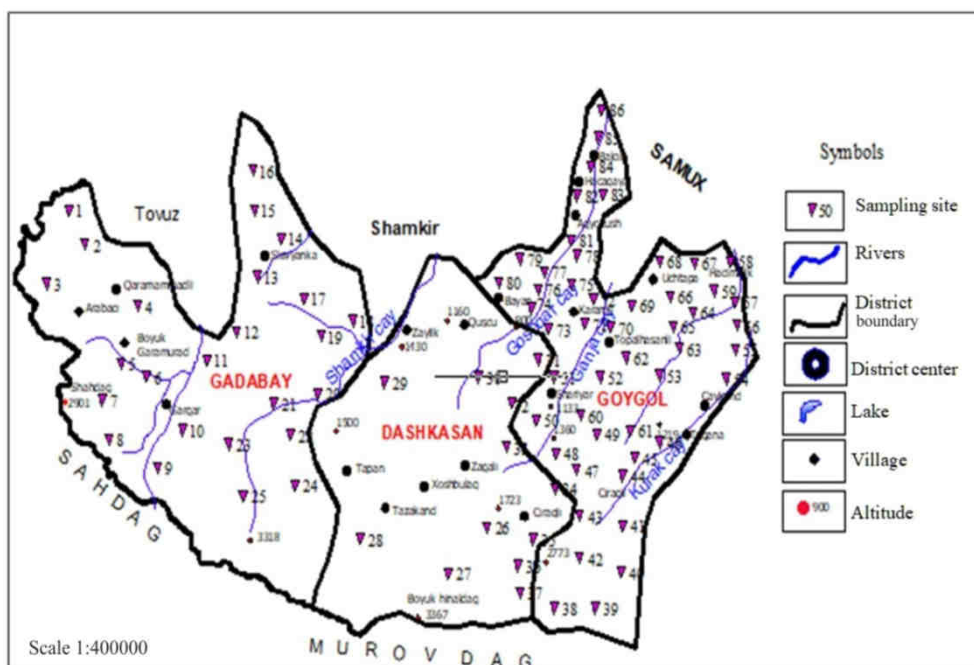


Fig. 1. The sampling map

Neutron activation analysis (NAA), atomic absorption spectroscopy (AAS) and particle-induced X-ray emission (PIXE) methods were used in the research. Research methods are based on the application of mosses as indicators, the amount of elemental pollutants in atmospheric sediments and their suitability in mosses. Besides, it reflects the general state of atmospheric pollution in the studied areas [33-40].

Sampling

The number of samples taken by moss species is given in Table 1.

Sample collection followed a standardised field protocol. A minimum grid density of 1.5 sampling points per 1000 km² was maintained, with higher densities permitted where finer spatial resolution of atmospheric deposition patterns was required.

Pleurozium schreberi was the preferred target species; where unavailable, *Hylocomium splendens* was used as a substitute. Other moss species may be employed provided their elemental uptake capacities and calibration coefficients relative to the primary species are established. Field campaigns were conducted between April and October to ensure optimal sample quality.

To minimise contamination from road traffic and human settlement, sampling sites were situated no closer than 300 m from major highways and built-up or industrial zones, and at least 100 m from minor rural roads and private structures. In densely urbanised areas, these minimum distances may be reduced to 100 m and 50 m, respectively. All sampling locations were confined to forested or wooded terrain; within such sites, open clearings or positions at least 3 m from tree trunks were preferred to eliminate canopy wash effects.

Table 1
Species composition of moss samples collected from the Goygol, Dashkasan, and Gadabay regions

Species	Goygol	Dashkasan	Gadabay
Total number of samples	50	5	31
<i>Pleurozium schreberi</i>	35	3	24
<i>Hylocomium splendens</i>	10	2	6
Samples containing both species	5	-	1

Collectors avoided bare soil patches and selected material growing on decomposing stumps, fallen logs, or needle litter. Composite samples were assembled from 5-10 sub-samples gathered within a 50 m × 50 m grid cell, with all sub-samples belonging to the same species. Each composite was sealed in a paper or plastic bag (approximate volume: 2 litres) to prevent cross-contamination during transport, and accompanied by a field record specifying GPS coordinates (Greenwich reference system) and collection time. Smoking at collection sites was prohibited, and only talcum-free disposable polyethylene gloves were permitted.

Within two weeks of collection, samples were re-bagged in paper and oven-dried; material not processed within this window was held under refrigeration. Laboratory handling was performed on inert surfaces (paper, glass, or polyethylene sheeting) in a dedicated clean room, with metal implements strictly excluded. Each sample was manually cleaned to remove forest litter and soil particles, retaining only the green and green-brown shoot segments; for *Hylocomium splendens*, only growth increments from the most recent three years were retained. Samples were not rinsed with water. Drying proceeded first at ambient temperature and then at 40 °C until constant mass was achieved, with all elemental concentrations subsequently referenced to this dry weight. Residual material was archived in paper bags for potential further analysis [41-44].

Sample preparation

Elemental quantification in moss specimens was performed through a combination of instrumental neutron activation analysis (INAA), particle-induced X-ray emission (PIXE), and atomic absorption spectrometry (AAS). Cadmium, copper, and lead concentrations were specifically determined via graphite furnace AAS using the flame atomisation technique.

Sample capsules were fabricated from polyethylene or aluminium, with fluoroplast or pure carbon employed in cases requiring greater chemical inertness. Up to seven capsules

could be loaded simultaneously into a single subchannel for irradiation. Following system upgrades, all mechanical handling operations became fully automated, allowing the entire irradiation sequence to be completed within 1.5 seconds without any manual contact with the samples. The REGATA irradiation facility incorporates four high-purity semiconductor detectors - both Ge and NaJ types - achieving a detection efficiency of 30 %. Within this system, the Ch1 subchannel is dedicated to long-lived radionuclides, while Ch2 handles short-lived species [45].

Sequential irradiation was carried out in two separate REGATA channels. For nuclides with half-lives measured in seconds, capsules were transferred directly into the detector assembly and irradiated without any intervening delay. Short-lived isotopes - specifically Al, I, Mg, Mn, Ti, and V - were activated for 3 minutes in Ch2 and immediately counted [46, 47]. Long-lived isotopes required extended activation in Ch1, with irradiation periods of approximately 4 days.

Post-irradiation counting was conducted in two distinct stages. In the first stage, carried out 4-5 days after irradiation, Sm was measured over 5 minutes, while As, Au, Br, Cd, La, Lu, Na, Mo, U, and W were counted over 1 hour. In the second stage, samples were held for a further 20-day decay period before a 3-hour counting session was performed to determine Ag, Ba, Ce, Co, Cr, Cs, Eu, Fe, Gd, Hf, In, Nd, Rb, Sb, Sc, Se, Sr, Ta, Tb, Th, Yb, Zr, and Zn.

Elemental concentrations were computed using specialised software developed at the NAA sector of JINR Dubna, incorporating the Genie-2000 programme (Canberra) as the core analytical platform [48-51].

Analysis

Neutron activation analysis of moss specimens was performed using the IBR-2 pulsed fast reactor located at the Frank Laboratory of Neutron Physics (FLNP, JINR, Dubna), following previously established procedures. For short-lived radionuclide determination, samples underwent irradiation for 3 minutes at a thermal neutron fluency rate of approximately $1.3 \cdot 10^{12} \text{ n cm}^{-2} \text{ s}^{-1}$. The resulting induced gamma activity was recorded on two occasions - each lasting 3 minutes - following a decay interval of 5-7 minutes [46].

Determination of long-lived isotopes was accomplished via a cadmium-screened irradiation channel operating at a resonance neutron fluency rate of approximately $1.6 \cdot 10^{12} \text{ n cm}^{-2} \text{ s}^{-1}$. Under these conditions, samples were irradiated for 89-90 hours, subsequently repacked, and measured after a decay period of 4-5 days, with each measurement lasting 45 minutes. Gamma activity detection was carried out using a Canberra Ge (HP) detector, characterised by a resolution of 1.9 keV at the ^{60}Co 1332 keV gamma line [34, 35].

Gamma spectral data were processed using dedicated software developed at JINR, which calculates elemental concentrations through a relative standardisation method. The certified reference materials employed for calibration included Trace Elements in Pine Needles - 1575a (NIST), Trace Elements in Coal - 1632b (NIST), Montana Soil - 2710 (NIST), and BCR-667 (Belgium). Spectral evaluation was further supported by analytical software developed at FLNP. To explore interelemental associations and reduce data dimensionality, factor analysis (FA) was applied. All statistical computations were executed using Stat-Soft™ Statistica 9 (StatSoft, Tulsa, OK, USA) [34, 35].

Results and discussion

When multiple observed variables share a common underlying cause, they are collectively referred to as latent variables - quantities that cannot be directly measured but whose influence manifests across a set of observable indicators.

To identify and characterise the principal sources of elemental pollution and to delineate the most contaminated zones, factor analysis (FA) was employed as the primary multivariate statistical tool. FA operates by compressing large data matrices into a reduced dimensional space through orthogonal factor transformations, thereby extracting interpretable underlying factors that account for the observed patterns of covariation.

Elemental concentrations were quantified across a total of 86 moss samples - 50 collected from the Goygol region and 36 from the combined Gadabay and Dashkasan territories - using an integrated analytical approach comprising NAA, PIXE, and AAS. The full suite of 44 elements determined comprised: Na, Mg, Al, Si, Cl, K, Ca, Sc, Ti, V, Cr, Mn, Fe, Co, Ni, Cu, Zn, As, Se, Br, Rb, Sr, Mo, Ag, Cd, In, Sb, I, Cs, Ba, La, Ce, Nd, Sm, Eu, Tb, Tm, Yb, Hf, Ta, W, Au, Th, and U.

Observed variables are explained by some common cause (or several causes). Thus, observable variables are called latent variables (variable values cannot be measured directly).

Correlation analysis was conducted to determine the dependence between different elements. Correlation coefficients, r were calculated using MS Excel and correlation matrixes were constructed for some element pairs:

- 1) high degree of interaction - $0.7 < r < 0.99$
- 2) high average degree of interaction - $0.5 < r < 0.69$
- 3) low degree of interaction - $0.2 < r < 0.49$.

There is a higher correlation between elements from the same source.

Simple statistical procedures were applied to explore interrelationships among the measured variables. Examination of the correlation matrix revealed strong mutual correlations among the majority of metals analysed. Particularly pronounced positive associations were observed between the following element pairs: Al-V ($r = 0.96$), Al-Ti ($r = 0.97$), Ti-V ($r = 0.94$), Fe-Co ($r = 0.96$), Cr-Fe ($r = 0.90$), Cr-Co ($r = 0.90$), Sc-Fe ($r = 0.99$), Sc-Co ($r = 0.97$), Sc-V ($r = 0.91$), Mg-Al ($r = 0.89$), Mg-Ti ($r = 0.87$), Al-Sc ($r = 0.89$), and Al-Cs ($r = 0.91$).

Noteworthy correlations were also recorded between Na and Al ($r = 0.88$), as well as between Na and a range of abundant transition metals - Sc, Ti, V, Cr, Fe, Co, Hf, and Ta - yielding coefficients of 0.91, 0.90, 0.85, 0.85, 0.90, 0.93, and 0.89, respectively. Similarly, Na exhibited meaningful associations with rare earth elements La, Ce, Sm, Tb, and Tm, with correlation coefficients of 0.85, 0.84, 0.86, 0.87, and 0.80, respectively.

Overall, the correlation structure confirms that rare earth elements are strongly intercorrelated and exhibit close statistical linkages with both Mg and Al, as well as with the transition metal group. Additional significant pairwise correlations were identified between Th-U ($r = 0.96$), Ta-U ($r = 0.96$), V-Th ($r = 0.92$), U-Hf ($r = 0.93$), and Hf-Th ($r = 0.96$).

Factor analysis, a branch of multivariate statistical analysis that combines methods for estimating the size of a set of observed variables by studying the structure of covariance and correlation matrixes, is based on the correlation hypothesis. Factor analysis was applied to identify the possible sources of elements in moss samples.

The factors represent groups of elements that are likely associated with crustal material, industrial emissions, mining activities, and vegetation influence, as interpreted from their high loadings. The following table summarises the elements, their loadings, probable sources, and brief explanations for each factor.

The four identified factors are interpreted in Table 2.

Table 2

Factor loadings of elements in moss samples and their probable sources

Factor	Element	Loading	Probable source	Notes / Explanation
F1	Cs	0.93	Crustal material	Soil particle contamination
	Sc	0.90	Crustal material	-
	Hf	0.86	Crustal material	-
	Al	0.82	Crustal material	-
	Fe	0.80	Crustal material	-
	Na	0.79	Crustal material	-
	Ba	0.72	Crustal material	-
	Co	0.70	Crustal material	-
	Mn	0.69	Crustal material	-
	Ti	0.66	Crustal material	-
	Tb	0.94	Rare earth element	Soil contamination indicator
	Yb	0.91	Rare earth element	-
	Tm	0.90	Rare earth element	-
	Sm	0.80	Rare earth element	-
	Ce	0.75	Rare earth element	-
	Nd	0.73	Rare earth element	-
	La	0.61	Rare earth element	-
	-	-	Fly ash	Possible source from solid fuel combustion
F2	As	0.73	Fuel burning / Mining	Toxic, carcinogenic; mainly fuel combustion and Cu/Au mines
	Ni	0.63	Mining / Regional geology	Similar to neighbouring Georgia
	Cr	0.62	Mining / Regional geology	-
	Mg	0.62	Soil chemistry	Related to Ni/Cr content and low Ca, K, Mo
	Th	0.61	Mining	High near gold/silver/copper plant
	U	0.72	Mining	High near gold/silver/copper plant
F3	Cu	0.63	Industrial	Metallurgical emissions, Ganja
	Rb	0.55	Industrial	-
	Cd	0.59	Industrial	-
	Au	0.69	Industrial	-
F4	Cl	0.89	Vegetation / Metal waste	Green areas influence
	K	0.86	Vegetation	-
	Zn	0.64	Metal waste	High at sites 10 & 24; near metal production/smelting

In this regard, factor analysis can be successfully applied to determine the possible sources of origin of certain elements in mosses. In works related to environmental assessment, the idea behind factor analysis is that correlations between several elements in mosses are determined by the presence of fewer independent factors.

The following results were obtained in this study:

1. The concentration of all elements in Dashkasan and Gadabay mosses is significantly higher than that in the mosses collected from Goygol area.
2. Factors characterising the element composition of Dashkasan and Gadabay mosses:
 - 1) burning of fossil fuels (Al, Sc, Ta, Tb, Th, Ce, La, Yb, Cr, Sm, U, Hf, As, Mg and Cs)
 - 2) biochemical processes in moss tissues (K, Ca, Cl, Sr, Br, Zn and Rb)
 - 3) geological factor (Na, Co, Ni, Cs and Ba)
 - 4) industrial cities (Cu, Mo, W, Cd)
 - 5) metallurgy (Mn, Zn, Ba, Ni, Cd)
 - 6) production of ferrovanadium (V, Fe)
 - 7) combustion of diesel fuel (Sb, Br)
 - 8) chemical industry (Cl, I)
3. Factors characterising the element composition of Goygol mosses:
 - 1) Soil erosion, solid fuel burning (Na, Al, Sc, Fe, As, La, Ce, Sm, Tb, Hf, Ta, Th and U)
 - 2) Industrial areas (W, Sr, Ba, Br, Cd, Ca Zn, Mg and Fe)
 - 3) Biochemical processes in moss tissues (Cl, K, Ca, Na, Mg, Zn and Sr)
 - 4) Metallurgy, processing, and industry in cities (Mo, Co, Mn and Fe)
 - 5) Processing and burning of petroleum and oil products (V, Ni)
 - 6) Plant factor (Cs, Rb)
 - 7) Production of building materials (Cr, Ni)
4. In most of the studied areas, the value of the total pollution coefficient corresponds to a low level of pollution. Medium and high pollution is observed in the areas adjacent to the main sources of pollution.
5. According to biomonitoring of atmospheric deposition of heavy metals in Europe, the level of concentrations of major pollutants in the Dashkasan and Gadabay regions is higher, while in the Goygol region, it is lower than the average European level (Fig. 2, Table 3).
6. For the first time, a database was compiled on the concentration of 44 elements, including heavy metals and actinoids, in mosses collected from the territories of the Western region of Azerbaijan (Goygol, Dashkasan, and Gadabay).

In Figure 2, the contamination maps of certain elements, such as Sc, Al, and Fe, are presented. Areas shown in green represent clean zones, whereas areas shown in red indicate polluted zones.

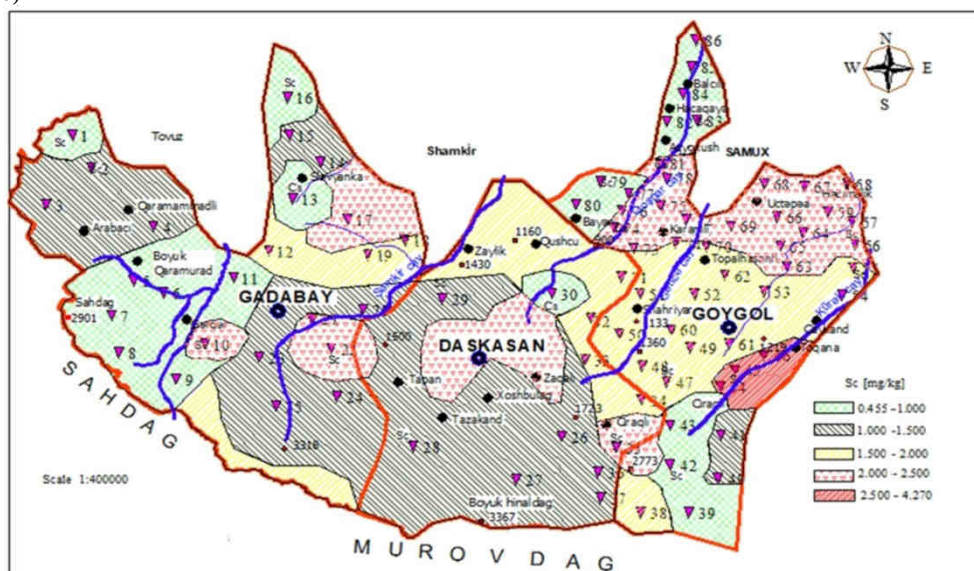
Table 3

Comparison of element concentrations in moss samples from Azerbaijan with Norwegian reference values and European background levels (ICP vegetation, dry weight basis [mg/kg])

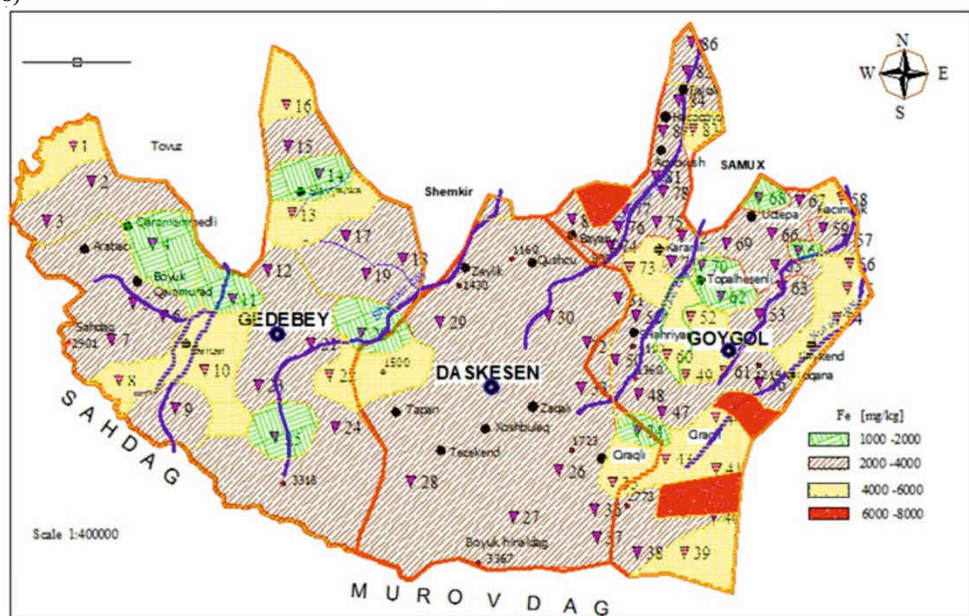
Element	Azerbaijan (2015) Median	Norway (2010) Median	European background ICP Vegetation (2010/2011) Mean	AZ / EU BG ratio	Assessment
Na	512.5	n/a	300	1.71	Elevated
Mg	3670	1730	2400	1.53	Elevated
Al	3870	200	2950	1.31	Slightly elevated (geogenic influence)
Cl	134	n/a	150	0.89	Comparable
K	5380	n/a	4600	1.17	Slightly elevated
Ca	9750	2820	6500	1.50	Elevated

Element	Azerbaijan (2015) Median	Norway (2010) Median	European background ICP Vegetation (2010/2011) Mean	AZ / EU BG ratio	Assessment
V	1.075	0.92	5.6	0.19	Low median; localised hotspots present
Mn	145	256	110	1.32	Elevated
Fe	2845	209	2000	1.42	Elevated
Zn	26.15	26.5	20.4	1.28	Elevated
As	1.015	0.093	0.70	1.45	Elevated
Br	5.325	n/a	5.1	1.04	Comparable (no full reference data available)
Mo	0.4435	0.135	0.29	1.53	Elevated
Cd	0.308	0.058	0.18	1.71	Strongly elevated
I	3.63	n/a	1.29	2.81	Elevated (regional variability)
La	1.745	0.189	1.6	1.09	Slightly elevated
Sm	0.29	0.33	0.18	1.61	Elevated
W	0.0758	0.127	0.10	0.76	Comparable / slightly lower
Au	0.00171	n/a	0.00004	42.75	Enriched (localised geological/mining influence)
U	0.1455	0.015	0.10	1.46	Elevated

a)



b)



c)

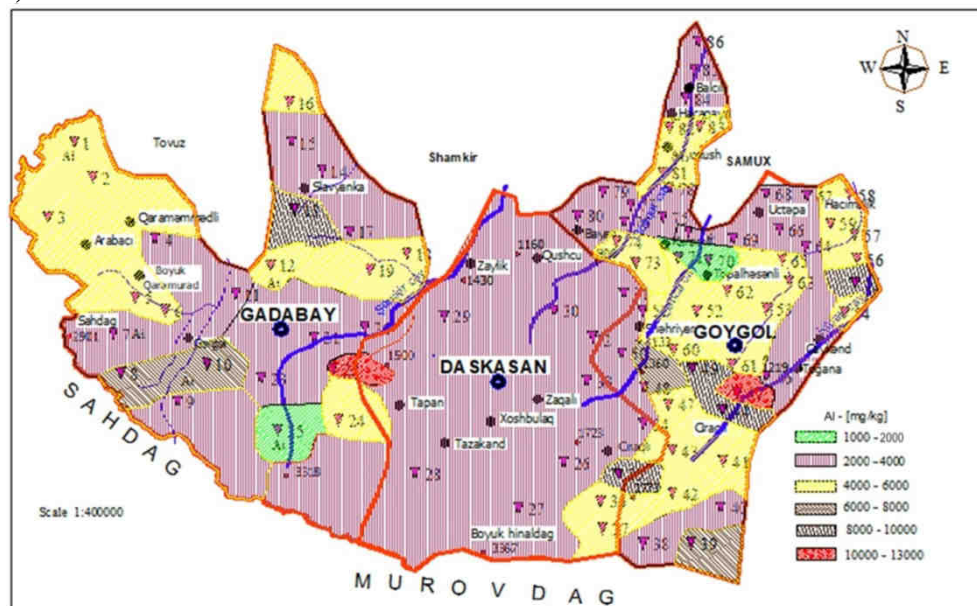


Fig. 2. Distribution maps of: a) scandium, b) iron, c) aluminium elements in the Dashkesan, Gadabay and Goygol regions of Azerbaijan

Conclusion

A comprehensive elemental dataset was established through the analysis of 86 moss samples - 50 from Goygol and 36 from Gadabay (31) and Dashkasan (5) - quantifying 44 elements (Na, Mg, Al, Si, Cl, K, Ca, Sc, Ti, V, Cr, Mn, Fe, Co, Ni, Cu, Zn, As, Se, Br, Rb, Sr, Mo, Ag, Cd, In, Sb, I, Cs, Ba, La, Ce, Nd, Sm, Eu, Tb, Tm, Yb, Hf, Ta, W, Au, Th, and U) via the combined application of NAA, PIXE, and AAS.

By integrating advanced elemental analysis of moss biomonitors with multivariate statistical interpretation (factor analysis) and GIS-based spatial modelling, the governing patterns of heavy metal distribution within atmospheric deposits across the Goygol, Dashkasan, and Gadabay territories were successfully characterised. The methodology demonstrated in this study is transferable and may be applied to assess atmospheric pollution in other industrially active and densely populated regions of Azerbaijan, thereby contributing to broader national environmental management efforts.

Markedly elevated elemental concentrations recorded in mosses from Dashkasan and Gadabay relative to those from Goygol underscore the significant role of local industrial enterprises and cumulative anthropogenic activities in shaping the regional atmospheric pollution landscape.

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References

- [1] Al-Alam J, Chbani A, Faljoun Z, Millet M. The use of vegetation, bees, and snails as important tools for the biomonitoring of atmospheric pollution: a review. *Environ Sci Pollut Res*. 2019;26(10):9391-408. DOI: 10.1007/s11356-019-04388-8.
- [2] Bibi D, Tözsér D, Sipos B, Molnár VÉ, Simon E, Tóthmérés B. Complex study of air pollution based on tree species in Vienna. *Air Qual Atmos Health*. 2024;17:417-24. DOI: 10.1007/s11869-023-01452-8.
- [3] Meng Y, Li R, Fu H, Bing H, Huang K, Wu Y, et al. The sources and atmospheric pathway of phosphorus to a high alpine forest in Eastern Tibetan Plateau, China. *J Geophys Res Atmos*. 2020;125:e2019JD031327. DOI: 10.1029/2019JD031327.
- [4] Wolterbeek HT. Biomonitoring of trace element air pollution: principles, possibilities and perspectives. *Environ Pollut*. 2002;120(1):11-21. DOI: 10.1016/S0269-7491(02)00124-0.
- [5] Brunialti G, Frati L. Biomonitoring with lichens and mosses in forests. *Forests*. 2023;14(11):2265. DOI: 10.3390/f14112265.
- [6] Harmens H, Norris D, Alber R, Aleksienak Y, Ashmore M, Jesús A, et al. Spatial and Temporal Trends in Heavy Metal Accumulation in Mosses in Europe (1990-2005). Centre for Ecology & Hydrology; 2008. ISBN: 9781855312395.
- [7] Monaci F, Ancora S, Paoli L, Loppi S, Franzaring J. Air quality in post-mining towns: tracking potentially toxic elements using tree leaves. *Environ Geochem Health*. 2023;45:843-59. DOI: 10.1007/s10653-022-01252-6.
- [8] UNECE CLRTAP. Manual on methodologies and criteria for modelling and mapping critical loads and levels and air pollution effects, risks and trends. 2015. Available from: <http://www.umweltbundesamt.de>.
- [9] Temmerman L, Bell NB, Garrec JP, Andreas K, Krause G, Tonneijck A. Biomonitoring of air pollutants with plants. 2001. Available from: <https://www.researchgate.net>.
- [10] Buse A, Norris D, Harmens H, Büker P, Ashenden T, Mills G, et al. Heavy metal concentrations in European mosses: 2000/2001 survey. *J Atmos Chem*. 2004;49:425-36. DOI: 10.1007/s10874-004-1257-0.

- [11] Harmens H, Norris DA, Steinnes E, Kubin E, Piispanen J, Alber R, et al. Mosses as biomonitors of atmospheric heavy metal deposition in Europe. *Environ Pollut.* 2010;158:3144-56. DOI: 10.1016/j.envpol.2010.06.039.
- [12] Chaudhuri S, Roy M. Global ambient air quality monitoring: can mosses help? *Environ Dev Sustain.* 2023. DOI: 10.1007/s10668-023-03043-0.
- [13] Lazo P, Kika A, Qarri F, Bekteshi L, Allajbeu S, Stafilov T. Air quality assessment by moss biomonitoring and trace metals deposition. *Aerosol Air Qual Res.* 2022. DOI: 10.4209/aaqr.220008.
- [14] Goryainova Z, Vuković G, Urošević MA, Vergel K, Ostrovnyaya T, Frontasyeva M, et al. Vertical distribution of elements using moss biomonitoring. *Atmos Pollut Res.* 2016;7(4):690-7. DOI: 10.1016/j.apr.2016.02.013.
- [15] Gerdol R, Marchesini R, Iacumin P, Brancaleoni L. Monitoring air pollution trends using mosses and lichens. *Chemosphere.* 2014;108:388-95. DOI: 10.1016/j.chemosphere.2014.02.035.
- [16] Aboul JR, Fernández JA, Boquete MT, Carballeira A. Sampling optimization in moss biomonitoring surveys. *Environ Pollut.* 2010;158(7):2209-14. DOI: 10.1016/j.envpol.2010.02.019.
- [17] World Health Organization. Ambient (outdoor) air pollution. Available from: [https://www.who.int/news-room/fact-sheets/detail/ambient-\(outdoor\)-air-quality-and-health](https://www.who.int/news-room/fact-sheets/detail/ambient-(outdoor)-air-quality-and-health).
- [18] Harmens H, editor. Heavy Metals, Nitrogen and POPs in European Mosses: 2020 Survey Manual. ICP Vegetation; 2020. Available from: <https://icpvegetation.ceb.ac.uk>.
- [19] ICP Vegetation. Heavy Metals in European Mosses: 2010 Survey Manual. CEH Bangor; 2010. Available from: <https://files.core.ac.uk/download/pdf/57335.pdf>.
- [20] Madadzada A, Nuhuyeva Sh, Mammadov E, Frontasyeva M, Sharifova M, Gasumov K, et al. Heavy metals in atmospheric precipitation of Goygol region. *Proc Int Conf.* 2019. DOI: 10.2991/isees-19.2019.18.
- [21] Madadzada A, Nuhuyeva Sh, Mammadov E, Frontasyeva M, Jabbarov NS, Strelkova L, et al. Atmospheric deposition in Azerbaijan using moss technique. *Ecol Chem Eng S.* 2022;29(2):143-53. DOI: 10.2478/eces-2022-0011.
- [22] Nuhuyeva Sh, Mammadov E. Heavy metals in precipitation of Azerbaijan regions. *Bull Sci Pract.* 2021;7(6):60-6. DOI: 10.33619/2414-2948/67/08.
- [23] Shetekauri S, Shetekauri T, Kvlividze A, Chaligava O, Kalabegishvili T, Kirkesali EI, et al. Preliminary results of atmospheric deposition of major and trace elements in the Greater and Lesser Caucasus Mountains studied by the moss technique and neutron activation analysis. *Ann Bot (Roma).* 2015;5:89-95. DOI: 10.4462/annbotrm-13066
- [24] International Atomic Energy Agency. Sampling and analytical methodologies for neutron activation analysis of airborne particulate matter. Available from: <https://www.iaea.org/publications/346>.
- [25] Jolliffe IT. Principal Component Analysis. 2nd ed. New York: Springer; 2002. ISBN: 0387954422.
- [26] Markert B, Wappelhorst O, Weckert V, Herpin U, Siewers U, Friese K, et al. The use of bioindicators for monitoring the heavy-metal status of the environment. *J Radioanal Nucl Chem.* 1999;240(2):425-9. DOI: 10.1007/BF02349387
- [27] Markert B, Wünschmann S, Fränzle S, Wappelhorst O, Weckert V, Breulmann G, et al. On the road from environmental biomonitoring to human health aspects: monitoring atmospheric heavy metal deposition by epiphytic/epigeic plants: present status and future needs. *Int J Environ Pollut.* 2008;32(4):486-98. DOI: 10.1504/IJEP.2008.018412.
- [28] Madadzada A, Badawy M, Hajiyeva S, Veliyeva Z, Hajiyeve O, Shvetsova M, et al. Atmospheric deposition in Baku using NAA and GIS. *Microchem J.* 2019;147:605-14. DOI: 10.1016/j.microc.2019.03.061.
- [29] Markert B, Friese K. Trace Elements: Their Distribution and Effects in the Environment. Amsterdam: Elsevier; 2000. ISBN: 0080543138.
- [30] Markert BA, Breure AM, Zechmeister HG, editors. Bioindicators and Biomonitors. Amsterdam: Elsevier; 2003. ISBN: 0080441777.
- [31] Zinicoscaia I, Chaligava O, Yushin N, Grozdov D, Vergel K, Hramco C. Moss biomonitoring of atmospheric trace elements in Moldova. *Arch Environ Contam Toxicol.* 2022;82:355-66. DOI: 10.1007/s00244-022-00918-7.
- [32] Nurulshyha MY, Azman AN. Moss as bio-indicator for air quality. *Int J Eng Adv Technol.* 2021;10(5):43-7. DOI: 10.35940/ijeat.E2579.0610521.
- [33] Nickel S, Schröder W, Schmalfuss R, Saathoff M, Harmens H, Mills G, et al. Modeling heavy metals in mosses across Europe. *Environ Sci Eur.* 2018;30:53. DOI: 10.1186/s12302-018-0183-8.
- [34] Ostrovnyaya TM, Nefedyeva LS, Nazarov VM, Borzakov SB, Strelkova LP. Software for INAA on the basis of relative and absolute methods using nuclear data base. In: Activation Analysis in Environment Protection. JINR Preprint D-14-93-325. Dubna, RF; 1993. p. 319-25. Available from: [https://www1.jinr.ru/Preprints/2002/137\(E14-2002-137\).pdf](https://www1.jinr.ru/Preprints/2002/137(E14-2002-137).pdf).

- [35] Rühling Å, Tyler G. Heavy metal deposition in Scandinavia. *J Appl Ecol.* 1971;8:497-507. DOI: 10.2307/2402886.
- [36] Berg T, Pedersen U, Steinnes E. Environmental indicators for long-range atmospheric transported heavy metals based on national moss surveys. *Environ Monit Assess.* 1996;43:11-7. DOI: 10.1007/BF00399567.
- [37] Świsłowski P, Kriz J, Rajfur M. Bark biomonitoring of heavy metals. *Ecol Chem Eng S.* 2020;27(2):195-210. DOI: 10.2478/eces-2020-0013.
- [38] Świsłowski P, Rajfur M, Waclawek M. Heavy metals and chlorophyll in mosses. *Ecol Chem Eng S.* 2021;27(4):591-601. DOI: 10.2478/eces-2020-0073.
- [39] Steinnes E, Jacobsen LB. Mosses as monitors in Arctic regions. *Norsk Polar Inst Rep.* 1994;88.
- [40] Słonina N, Świsłowski P, Rajfur M. Mosses in aerosol studies. *Ecol Chem Eng S.* 2021;28(2):163-72. DOI: 10.2478/eces-2021-0012.
- [41] Wu R, Yao F, Li X, Shi C, Zang X, Shu X, et al. Manganese pollution and remediation strategies. *Microorganisms.* 2022;10:2411. DOI: 10.3390/microorganisms10122411.
- [42] Shetekauri S, Chaligava O, Shetekauri T, Kvlividze A, Kalabegishvili T, Kirkesali E, et al. Biomonitoring air pollution using moss in Georgia. *Pol J Environ Stud.* 2018;27(5):2259-66. DOI: 10.15244/pjoes/73798.
- [43] Steinnes E, Berg T, Uggerud HT. Spatial patterns and temporal trends of heavy metal concentrations in moss and surface soil specimens collected in Norway between 1990 and 2010. *Environ Sci Eur.* 2014;26:27. DOI: 10.1186/s12302-014-0027-y.
- [44] Steinnes E, Hanssen J, Rambæk JP, Nills B. Heavy metals in Norway mosses. *Water Air Soil Pollut.* 1994;74:121-140. DOI: 10.1007/BF01257151.
- [45] Tyler G. Moss analysis method. In: *Clean Air Congress Proc.* Academic Press; 1970. DOI: 10.1016/B978-0-12-239450-8.50032-0.
- [46] Dmitriev AY, Pavlov SS. Automation of quantitative determination of elemental content using neutron activation analysis at the IBR-2 reactor. *Phys Part Nuclei Lett.* 2013;10:33-6. DOI: 10.1134/S1547477113010056.
- [47] Frontasyeva MV, Pavlov SS. Analytical investigations at the IBR-2 reactor in Dubna. *JINR Preprint E14-2000-177*; 2000. Available from: <https://rusist.info/book/2159866>.
- [48] Zechmeister HG. Heavy metal deposition in Alps. *Int J Environ Pollut.* 1995;89(1):73-80. DOI: 10.1016/0269-7491(94)00042-C.
- [49] Gómez-Ensastegui C, Avila-Pérez P, García-Rivas JL, Barrera-Díaz EC, Huemantzin BH, Ortiz-Oliveros BH, et al. Evaluation of an aquatic liverwort and terrestrial moss as biomonitors of heavy metals associated with particulate matter. *Sci Rep.* 2025;15:4127. DOI: 10.1038/s41598-025-88348-y.
- [50] Chaligava O, Zinicovscaia I, Cepoi L. Environmental drivers of trace element variability in *Hypnum cupressiforme*: a cross-regional moss biomonitoring study. *Plants.* 2025;14(13):2040. DOI: 10.3390/plants14132040.
- [51] Rajfur M, Plášek V, Zinicovscaia I, Yushin N, Jerz D, Świsłowski P. Preliminary findings from a pilot moss biomonitoring study in Patagonia region. *Sci Rep.* 2025;15:25295. DOI: 10.1038/s41598-025-11421-z.