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Original scientific paper

MOSS BIOMONITORING OF AIR POLLUTION AND ASSESSMENT OF THE EFFECTS ON ARCHEOLOGICAL OBJECTS IN STOBI, NORTH MACEDONIA

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A b s t r a c t: The contents of 33 elements (Ag, Al, As, B, Ba, Be, Bi, Ca, Cd, Co, Cr, Cu, Fe, Ga, Ge, K, Li, Mg, Mn, Mo, Na, Ni, P, Pb, Pd, S, Sb, Se, Sn, Sr, Ti, V, and Zn) were determined in moss samples collected from 20 different locations in the ancient town of Stobi, North Macedonia. Determination was performed by the application of inductively coupled plasma with mass spectrometry (ICP-MS) after microwave digestion. It was found that the median values for the content of macroelements (Al, Ca, Fe, K, Mg) and for some specific trace elements (Co, Cr, Cu, Ni, Pb, and Zn) in moss samples from the Stobi site are higher to those obtained for the moss samples collected from the whole territory of North Macedonia. This significant increase in the contents of these elements is especially noticeable in the samples of moss taken from the monuments in Stobi, whose substrate is the mortar between lime and sandstones or sandstone, and in some cases when the substrate is a marble. Similar behavior has been observed also from the data for the median and the range of the content of these elements in the six moss samples collected from the wider vicinity of Stobi which have a noticeable increase in the median values of Ca, Co, Cr, Fe, Ni, Sr, and Zn compared to the median for the samples taken from the entire territory of North Macedonia. It was concluded that the contamination of the moss samples from Stobi, apart from the substrate from which they were taken, is also affected by the distribution of dust from the surrounding soils, in which the content of elements with increased contents is significantly higher than the average for soils from the entire territory of North Macedonia.

Key words: air pollution; moss biomonitoring; Stobi; North Macedonia

INTRODUCTION

The environmental pollution at hazardous levels for living organisms presents a global problem, and macro-case to monitor. Some sub-disciplines occurred with time to consider the realistic environmental conditions. Arguably, the understanding of atmospheric pollution is one of the more emergent areas of environmental science. Atmospheric pollution represents solutions or suspensions of minute amounts of harmful compounds in the air (Vallero, 2008). The degree and extent of environmental changes over the last decades have given new urgency and relevance to the detection and understanding of environmental changes, due to human activities, which have altered the global biogeochemical cycling of heavy metals and other pollutants (Agarval, 2009; Blagnytė and Paliulis, 2010). Monitoring toxic air pollutants is needed for understanding their spatial and temporal distribution and ultimately minimizing their harmful effects. In addition to direct physical and chemical methods of air pollution monitoring, bioindication has also been used to evaluate air pollution risk (Hock and Seifert, 2003; Vallero, 2008).

Heavy metals present only a part of a plurality of harmful compounds in the air. The degree of metals' extent and distribution in the air depends on the

frequency of the emission (Longchurst and Brebbia, 2013). However, the higher contents of certain heavy metals introduced in the air provide hazardous conditions for populations and the environment. Air pollution with heavy metals presents a global problem, but the hot spots occur and influence the local level (Gauderman et al., 2000, 2004; Harmens et al., 2010). For that issue, a double type of monitoring program should be applied. The first one should cover the larger areas, locating the hot spots in the investigating region; hence the small area where the local emission sources of heavy metals directly influenced the local population and its environment.

Mosses have been frequently used to monitor time-integrated bulk deposition of metals as a combination of wet, cloud, and dry deposition (Markert et al., 2003). Ectohydric mosses in particular draw negligible amounts of water and minerals from the soil and instead depend almost entirely on atmospheric inputs of nutrients (Rühling and Tyler, 1968). Because mosses have a high cation exchange capacity (CEC), they act as hyper-accumulators of metals and metal complexes. The metals are bound to the tissue with minimal translocation within the plant due to a lack of vascular tissue (Rühling and Tyler, 1968). This results in biological tissue that can be analyzed to reveal time-integrated deposition (Zechmeister et al., 2003). Additional advantages of using mosses as heavy metal biomonitors include their stationary nature, widespread geographic distribution, and low genetic variability between populations. It has been shown, that there is some experimental error due to heterogeneity in morphological characteristics and microenvironments among different populations (Zechmeister et al., 2003). There is also an incomplete understanding of the degree of mineral uptake by mosses in direct contact with the substrate (Gjengedal and Steinnes, 1990). Despite the accuracy and precision of precipitation analysis techniques, however, mosses offer an efficient, low-cost complement for determining metal concentrations at a large number of locations and offer analyses of biologically relevant fluxes at multiple scales.

Since 2000 the European moss survey has been conducted by an ICP Vegetation programme (http://icpvegetation.ceh.ac.uk/). In the frame of this programme, a heavy metal air pollution study was conducted also in North Macedonia, covering all the areas of the country, starting in 2002 by using mosses as biomonitors. Those studies were repeated in 2005, 2010, 2015, and 2020 (Stafilov et al., 2018; Barandovski et al., 2020). The first results suggest that the most important emission sources of potentially toxic elements (PTEs) are mines and smelters and therefore moss air pollution biomonitoring studies were focused on individual critical regions in the country, such as copper mines (Balabanova et al., 2010, 2016), ferronickel smelter plant (Bačeva et al., 2012), Pb–Zn mines and flotation plants (Angelovska et al., 2016; Balabanova et al., 2016) or As–Sb–Tl mine (Bačeva et al., 2013).

The effects of air pollution on cultural heritage have been the subject of numerous studies, with ever-increasing interest. Various anthropogenic activities including industry and traffic are the most important sources of air pollutants and they directly affecting also cultural heritage (Camuffo et al., 1982; Mitsos et al., 2022). The state of preservation of built heritage in urban environments gives rise to concerns about their future and demand for preservation actions. Air pollution, especially when matched with preferable climatic conditions, can lead to a significant reduction in the lifespan of materials and coatings (Ivaskova et al., 2015) or lead to structural degradation and color change (Sabbioni et al., 2003; Prieto-Taboada et al., 2013; Ozga et al., 2014).

This study aims to assess the effect of eventual air pollution on the cultural monuments in the ancient archeological site of Stobi, North Macedonia, to identify the main pollutants participating in the deterioration process and infer the origins of the pollutants. Also, the approach serves to evaluate the state of preservation of the external surface of the monuments in its environment, and therefore help devise future preventive conservation strategies, also in the context of pollution current status, and foreseen mitigation measures.

MATERIALS AND METHODS

Study area

The archeological site Stobi is an ancient city located in the southern part of North Macedonia. Its urban part is located on three terraces, which descend towards Crna Reka river, surrounded by walls, and at the mouth between Crna Reka and Vardar river. The main roads that connected the areas on the Danube with the Mediterranean countries passed in the vicinity of the city since the prehistoric period. Along this main road on the Balkan Peninsula, cultural influences moved from the south to the

north and vice versa. In the Roman period, an important road led along the Crna river, which connected the town of Stobi with the road *Via Ignatia* near Heraclea Lynkestis, near today's Bitola. Thus, the city of Stobi occupied a very important strategic, military and commercial position in the ancient period (Koteski and Jakovlev, 2016–2017).

Stobi lies on the Vardar river, about 30 km from the Greek border (Figure 1). During Hellenistic, Roman, and early Byzantine times, it was an important provincial center in northern Macedonia, a transition zone between Greek and Roman cultural influences, and an outpost lying between civilized Greece to the south and cruder tribes in the mountainous region to the north. Stobi already was a townsite at about the time of Alexander the Great (fourth century B.C.) and was then included within the Kingdom of Macedonia (Folk, 1975).

Fig. 1. A map of North Macedonia with the location of Stobi (red colored circle)

The prosperity of the city is particularly visible through the palaces and basilicas, decorated with frescoes and mosaics, which for the most part come from the 5th century, the time of the highest prosperity and importance of Stobi when it became the capital of the newly formed province of Macedonia Secunda. The new city was built in a short time on an area eight times larger than the previous settlement. In Stobi, a 4th-century synagogue was found over the remains of a 3rd-century synagogue (Hengel, 1966). In 146 B.C. Macedonia fell to the Roman Empire, and, by the first to third centuries A.D., Stobi became a very important city. A Roman theater large enough to seat 7,000 persons was built of marble about 200 A.D. By the fifth century Stobi was the seat of the bishopric, and at least five Christian basilicas were in the city and immediate surrounds (Wiseman and Mano-Zissi, 1973). Reaching its zenith about A.D. 400–500, Stobi went into rapid decline, and nothing more was built there after 600 by which time it seems to have been abandoned (Wiseman and Mano-Zissi, 1971, 1976; Wiseman, 1978, 1992).

The first written documents mentioning Stobi were recorded in the 19th century by Von Hahn (1861, 1869), Heuzey (1873), and Heuzey and Daumet (1876). During World War I, the German officer Dr. Hald started the first systematic excavations of the site (Hald, 1917). Since 1918, the excavations were coordinated by the architect F. Krischen who discovered the Cemetery Basilica and parts of the Episcopal Basilica. Between the two World Wars, Stobi was systematically excavated by the National Museum of Belgrade together with the Austrian, German and Danish archeologists (Pavlovski, 2013; National Institution Stobi, 2022). During this period many important archeological sites in Stobi were excavated (Theatre, Episcopal Basilica, Bishops' residence, Via Sacra, Porta Heraclea, Domus Fulonica, North Basilica, Central Basilica, and Synagogue, House of Psalms, etc.).

Stating in 1955 the investigation continued by the Archeological Museum in Skopje and the Institute for protection of Cultural Monuments of Macedonia excavating the North and Civil Basilicas and many other important sites in Stobi. In the 1970s the National Museum in Veles and the experts from the University of Austin started large excavations in Stobi leaded by James Wiseman, Mano-Zissi, and Blaga Aleksova (Wiseman and Mano-Zissi, 1971, 1976; Wiseman, 1978, 1992; Aleksova, 1981a,b,c, 1983, 1997, 2006). Further research on the Stobi site has been carried out through the continuous work of experts on the realization of a large number of projects implemented by the Museum of Macedonia, the National Institute for Protection of Cultural Monuments, and the National Institution Stobi, with many significant discoveries as well as conservation and protection of the findings discovered so far. These projects are mainly managed by Zoran Georgiev, Eleonora Petrova, Mila Shurbanovska, Silvana Blazhevska, Jovan Radnjanski, Momchilo Trajkovski, and Dragan Vergovski (National Institution Stobi, 2022).

According to the data given by Rakićević et al. (1965) and Stafilov et al. (2008, 2010), the surroundings of the archeological site Stobi are mainly part of the geology of the Upper Eocene sediments

which are quite represented in this part of the Tikveš basin. According to the lithological composition and position within the sedimentary formation, these sediments are divided into the following zones and subzones: flysch built from conglomerates with different lithological compositions, lower zone of flysch, lower zone of yellow sandstones, upper zone of flysch (gray sandstones, marls, and clays, yellow sandstones).

Moss sampling

Moss sampling was done from the 20 sampling sites in the archeological town of Stobi. The scheme of the Stobi with sampling locations is presented in Figure 2 and described in Table 1. The moss species are in general *Orthotrichum anomalum* which is typical small cushion-forming moss and it likes exposed, sunny situations on lime-rich walls and another masonry (Papp and Erzberger, 2012; Jang, 2020) used in some cases as an air biomonitor (Papp and Erzberger, 2012; Plášek et al., 2014; Zechmeister et al., 2019). Moss samples were collected from the surface of the archeological monuments, then cleaned from the attached litter or material from the substrate on which the moss is found, and then placed in a separate laboratory paper and turned several times until the moss was dried to room temperature to reach constant weight. To avoid contamination, non-talcum plastic disposable gloves were used and the mosses were handled on clean laboratory paper. No metal tools were used. The moss samples were stored in a dry place, at room temperature. Then, the moss samples were firstly subjected to physical preparation in terms of cleaning, including removal of other plant species and small organisms that are trapped in the moss plant body. Furthermore, the representative samples were dried to a constant temperature. Considering that some of the samples are rock mosses, the dry parts of the tissue were additionally sifted through a polyethylene sieve, to remove the mineral fraction from the base on which the plant tissue has been developed

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Sampling sites description

No.	Site description	Material
1	Arched building – North wall	Sandstone
2	North basilica – North wall	Sandstone
3	Civil basilica – North wall	Mortar between stones (lime+sand)
4	South wall of narthex – (Polyharmos)	Sandstone
5	Big bath – South wall	Sandstone
6	House of Peristerius – East wall	Mortar between stones
7	Theodosian palace – North corridor	Sandstone
8	Casino – South wall	Mortar between stones
9	Theater – East wall on stage	Marble
10	Theater – auditorium, row 10; Central part – west wing	Marble
11	Theater – auditorium, row 10; Central part – west wing	Marble
12	Theater – auditorium, row 9, Central part – southwest	Marble
13	Theater – auditorium, row 9, stairs along the western analemma	Marble
14	Episcopal basilica – North perimeter wall	Mortar between stones
15	Episcopal basilica – West wall of the narthex	Mortar between stones
16	Domus fulonica – South wall	Sandstone
17	Gate of Heraclea	Sandstone
18	A defensive tower from a late ancient defensive wall	Sandstone
19	South defensive wall	Mortar between stones
20	Temple of Isis	Sandstone

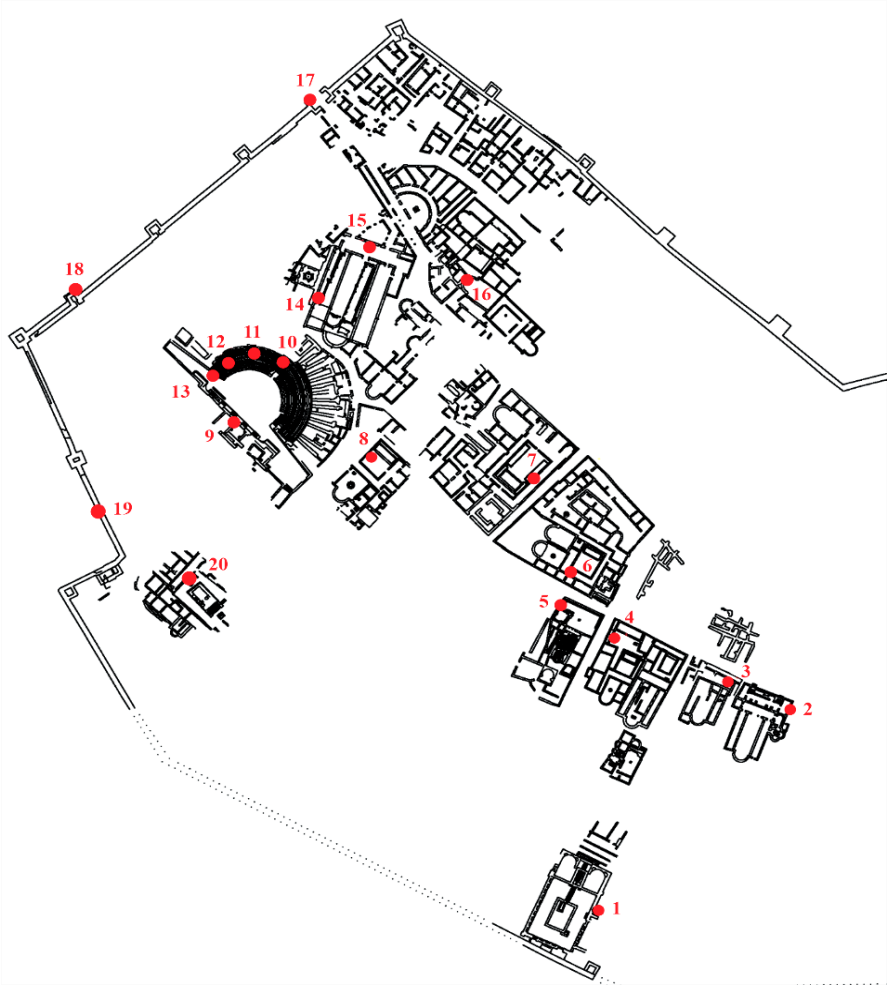

Fig. 2. Scheme of Stobi with the location of the sampling sites

Sample digestion and chemical analysis

All the moss samples were sent to one laboratory for further chemical analysis. Moss samples of around 0.5 g were placed in teflon digestion vessels; 5 ml HNO_3 (69 %, m/V) and 2 ml H_2O_2 (30 %, m/V) were added, and the vessels were placed in the rotor of the microwave digestion system (MARS 5, CEM Corporation, USA). The samples are digested until the complete combustion of the solid plant tissue. The digested solution has been transferred in a volumetric flask of 25 ml as the final dilution of the sample. The concentrations of 33 elements (Ag, Al, As, B, Ba, Be, Bi, Ca, Cd, Co, Cr, Cu, Fe, Ga, Ge, K, Li, Mg, Mn, Mo, Na, Ni, P, Pb, Pd, S, Sb, Se, Sn, Sr, Ti, V, and Zn) in digested sample solutions were determined by inductively coupled plasma with mass spectrometry (ICP-MS, 7850, Agilent Technologies). Additionally, the sensitivity was improved with the application of the He-collision cell gas line for minimizing the isotopic interferences. Sensitivity (as Mcps/ppm) was improved in several points ^{7}Li, ^{59}Co, ^{88}Y, ^{205}Tl, and ^{238}U. Optimal sensitivity was obtained for scanned isotopes: 55 Mcps, 400 Mcps, 320 Mcps, 700 Mcps, 250 Mcps, and 720 Mcps per 1 ppm, respectively. Oxides ratio CeO/Ce was <1.5%, while doubly charged ions Ce^{2+}/Ce were less than 2.5%. For quantitative analysis of elements concentration, calibration series of standard solutions were prepared for the analyzed elements in the range 1 ppb to 100 ppb for the trace elements and 0.1 ppm to 10 ppm for the macroelements. A standard solution of indium (^{115}In isotope was the measurement point) at a concentration of 10 ppb was used as an internal standard for calibration curve correction. The general instrumental specification and conditions of the system are given in Table 2. Furthermore, two reference materials (plant sample – BIPEA herbed mix ser. No. 2-5232-0010 and BCR-060 plant *Lagarosiphon major*) have been used to improve the accuracy of the measurements. The recoveries for the certified contents ranged from 88 to 109%.

T a b l e 2

Instrumental specification and condition of ICP-MS

Peristaltic pump	10-roller, 3 channels
Nebulizer	MicroMist (borosilicate glass)
Spray chamber	Scott-type double-pass (quartz)
Torch	Dimension 2.5 mm id injector, ShieldTorch system. Horizontal and vertical position: ±2 mm, in 0.1 mm steps. Sampling depth: 3 to 28 mm, in 0.1 mm steps.
Ion lens	Extraction lens, off-axis omega lens
Octopole reaction system	He collision cell gas line
Mass analyzer	Quadrupole, frequency 3 MHz hyperbolic rod profile with mass range 2–260 u
Vacuum system	Three-stage differential vacuum system
Isotope ratio, precision $^{107}Ag/^{109}Ag$	<0.05% RSD
Stability 20 min/2 h	< 2.0% RSD /< 3.0% RSD
Background *m/z* 9	< 0.2 cps
Interference reduction factor (performed in a matrix of 2% HNO_3 + 0.5% HCl) $^{59}Co/^{51}ClO$	➢ 30

RESULTS AND DISCUSSION

Data from the descriptive statistics of the measurements of 33 elements determined by ICP-MS (Ag, Al, As, B, Ba, Be, Bi, Ca, Cd, Co, Cr, Cu, Fe, Ga, Ge, K, Li, Mg, Mn, Mo, Na, Ni, P, Pb, Pd, S, Sb, Se, Sn, Sr, Ti, V, and Zn) in moss samples collected from 20 sampling locations in the ancient town Stobi are presented in Table 3. Data for the content of Al, Ca, Fe, K and Mg are given in % and for the content of the other elements in mg/kg. The values for these macroelements are in the following ranges: 0.28–5.22% Al; 0.044–0.70% Ca; 0.33–1.19% Fe; 0.10–0.48% K; 0.17–0.80% Mg. The high matrix content of these elements mostly originated from plant tissues and it can sometimes enrich the actual values from the atmospheric distribution of the particles reach in these elements and/or from the substrate on which the mosses are found. From the results shown in Tables 3 and 4, it can be seen that the results for the contents of the other analyzed elements (As, Ba, Cd, Mn, Mo, Na, Sr, and V) in the moss samples from Stobi are very similar to those obtained for the moss samples taken to the entire territory of North Macedonia.

In Table 4 a comparison of the median, minimal and maximal values for the content of analyzed elements in moss from Stobi with those for the Republic of Nortth Macedonia and those calculated from the data of six samples collected from locations within a radius of 30 km from Stobi (Stafilov et al., 2018). It could be seen that the median values for the content of macroelements (Al, Ca, Fe, K, Mg) and for some specific elements (Ca, Co, Cr, Cu, Fe, Ni, Pb, and Zn) in moss samples from the Stobi are higher to those obtained for the moss samples collected from the whole territory of North Macedonia. This significant increase in the contents of these elements is especially noticeable in the samples of moss taken from the monuments in Stobi, whose substrate is the mortar between lime and sandstones (sample No. 6, 8) or sandstone (No. 17 and 18), and in some cases and when the substrate is marble (10 and 11). Thus, the median content of Ca in moss samples from the Stobi site is 0.13% ranging from 0.04 to 0.7%, for Co is 5.47 mg/kg ranging from 2.19 to 12.7 mg/kg, for Cr is 43.1 mg/kg ranging from 17.3 to 124 mg/kg, for Cu is 11.6 mg/kg ranging from 6.6 to 27.4 mg/kg, for Fe is 0.66% ranging from 0.33 to 1.19%, for Ni is 103 mg/kg ranging from 54.4 to 300 mg/kg, for Pb is 22.3 mg/kg ranging from 10.2 to 58 mg/kg, and for Zn is 70.7 mg/kg ranging from 38 to 122 mg/kg. On the other hand, the content of these elements in moss samples taken from the entire territory of N. Macedonia is several times lower (exceppt Ca): the median content for Co is 0.60 mg/kg ranging from 0.16 to 2.00 mg/kg, for Cr is 5.7 mg/kg ranging from 1.8 to 31 mg/kg, for Cu is 4.6 mg/kg ranging from 3.0 to 8.3 mg/kg, for Fe is 0.17% ranging from 0.05 to 0.46%, for Ni is 3.5 mg/kg ranging from 0.68 to 63 mg/kg, for Pb is 4.9 mg/kg ranging from 2.2 to 14 mg/kg, and for Zn is 30 mg/kg ranging from 12 to 66 mg/kg.

T a b l e 3

Data for the content of the analyzed elements in all moss samples with general statistical data

Elements	Unit	Location No																			
		1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20
Ag	mg/kg	0.030	0.004	0.043	2.14	0.054	0.063	0.075	0.026	0.04	0.025	0.18	2.27	0.037	0.003	0.029	0.026	0.031	0.76	0.18	0.22
Al	%	0.65	0.35	0.28	0.41	0.55	1.07	0.52	0.78	0.57	0.74	1.19	0.33	0.51	0.39	0.54	0.47	0.77	1.02	1.34	5.22
As	mg/kg	0.34	0.26	0.17	0.25	0.23	0.98	0.19	0.40	0.41	0.33	0.50	0.16	0.27	0.21	0.30	0.21	0.54	0.90	0.62	0.89
B	mg/kg	6.11	2.26	5.64	4.45	2.34	13.9	0.39	27.4	2.90	10.1	15.7	2.08	7.30	4.07	3.00	14.6	13.4	18.3	16.4	26.5
Ba	mg/kg	36.0	24.2	22.0	21.6	33.9	74.6	46.9	66.4	65.7	42.3	64.5	33.9	33.1	21.6	39.6	30.6	62.0	197	81.3	82.1
Be	mg/kg	0.091	0.057	0.041	0.054	0.10	0.15	0.11	0.11	0.079	0.10	0.16	0.047	0.072	0.054	0.069	0.069	0.10	0.15	0.18	0.21
Bi	mg/kg	0.40	0.10	0.088	0.093	0.088	0.16	0.057	0.14	0.075	0.20	0.14	4.23	0.11	0.072	0.089	0.089	0.14	0.089	0.12	0.16
Ca	%	0.12	0.058	0.044	0.045	0.080	0.15	0.44	0.14	0.33	0.32	0.18	0.12	0.12	0.062	0.11	0.092	0.22	0.70	0.43	0.17
Cd	mg/kg	1.11	0.62	0.96	0.78	0.84	0.45	0.11	0.64	0.43	0.70	1.12	0.68	1.05	0.58	0.57	0.71	0.70	0.17	0.22	0.92
Co	mg/kg	7.87	4.58	3.16	5.11	4.59	12.72	5.62	7.66	4.46	5.32	8.90	2.19	4.24	3.59	8.83	3.60	8.76	5.67	8.23	8.43
Cr	mg/kg	59.9	36.9	24.8	43.3	37.3	124	17.3	63.9	40.9	49.7	69.0	23.8	35.5	34.4	42.9	31.6	75.2	58.1	65.4	65.1
Cu	mg/kg	12.2	6.72	6.60	6.68	8.44	14.7	14.4	17.1	10.4	12.6	19.0	8.51	11.0	6.80	10.9	9.82	18.0	13.3	17.7	27.4
Fe	%	0.73	0.43	0.33	0.46	0.54	1.11	0.51	0.75	0.62	0.70	1.10	0.34	0.57	0.43	0.70	0.45	0.86	0.93	1.15	1.19
Ga	mg/kg	1.69	0.85	0.66	0.99	1.320	2.95	1.08	2.15	1.30	1.87	2.99	0.78	1.24	0.96	1.36	1.16	2.02	2.54	3.82	3.89
Ge	mg/kg	1.13	0.64	0.56	0.77	0.89	1.95	0.69	1.39	1.03	1.23	1.73	0.61	0.94	0.73	1.16	0.82	1.32	1.59	1.94	2.05
K	%	0.26	0.14	0.11	0.10	0.16	0.34	0.23	0.35	0.22	0.36	0.45	0.39	0.34	0.15	0.20	0.30	0.46	0.36	0.46	0.48
Li	mg/kg	4.68	2.99	2.22	3.78	4.00	7.66	6.52	5.71	5.57	5.73	9.39	2.27	4.14	3.18	4.75	3.35	7.07	9.02	10.6	9.40
Mg	%	0.31	0.21	0.17	0.23	0.26	0.80	0.64	0.46	0.48	0.43	0.59	0.22	0.34	0.21	0.33	0.31	0.61	0.75	0.70	0.60
Mn	mg/kg	163	109	141	153	183	333	265	268	214	232	381	103	188	125	200	133	360	373	408	340
Mo	mg/kg	0.12	0.05	0.054	0.041	0.050	0.134	0.012	0.171	0.074	0.087	0.13	0.084	0.098	0.059	0.083	0.15	0.19	0.21	0.084	0.117
Na	mg/kg	97.8	103	72.7	97.9	125	250	102	171	175	222	155	149	181	106	138	113	223	207	282	247
Ni	mg/kg	204	120	74.7	120	96.1	300	80.2	163	72.4	123	159	54.4	88.2	93.8	103	85.5	164	65.3	103	129
P	mg/kg	194	133	118	77.7	127	253	246	318	335	392	544	448	411	122	244	175	582	419	547	446
Pb	mg/kg	27.6	20.2	18.6	23.7	26.8	22.0	29.8	21.9	15.1	18.7	31.0	13.3	28.8	16.6	46.5	16.1	22.6	10.2	36.1	58.0
Pd	mg/kg	0.010	0.010	0.008	0.008	0.010	0.021	0.018	0.015	0.017	0.016	0.015	0.008	0.01	0.008	0.011	0.010	0.016	0.027	0.031	0.019
S	mg/kg	1494	1194	1112	1093	1066	1529	1048	1669	1382	1547	1596	1649	1476	1143	1234	1577	1975	1560	1323	1055
Sb	mg/kg	0.090	0.020	0.081	0.041	0.032	0.014	0.005	0.048	0.055	0.069	0.07	0.12	0.1	0.033	0.072	0.057	0.072	0.031	0.020	0.024
Se	mg/kg	0.04	0.02	0.027	0.030	0.032	0.067	0.025	0.062	0.037	0.053	0.053	0.022	0.042	0.025	0.035	0.036	0.050	0.061	0.066	0.078
Sn	mg/kg	0.65	0.14	0.25	0.41	0.54	0.56	0.16	0.74	0.30	0.95	0.81	0.36	0.26	0.33	0.87	0.47	0.76	0.42	0.84	0.85
Sr	mg/kg	44.6	20.0	19.0	23.0	32.3	97.5	113	56.4	83.3	63.3	42.0	34.9	43.1	38.9	39.4	54.8	81.7	154	155	63.1
Ti	mg/kg	19.7	8.78	10.2	5.69	7.91	5.55	2.09	7.16	3.89	8.85	22.6	10.8	28.6	5.11	4.32	9.78	4.44	3.39	2.84	15.7
Tl	mg/kg	0.10	0.03	0.016	0.034	0.042	0.13	0.042	0.086	0.043	0.074	0.14	0.014	0.062	0.032	0.064	0.047	0.107	0.20	0.17	0.29
V	mg/kg	0.37	0.19	0.15	0.18	0.20	0.44	0.09	0.33	0.19	0.26	0.37	0.13	0.20	0.18	0.22	0.24	0.35	0.37	0.42	0.48
Zn	mg/kg	88.4	66.9	58.7	57.7	59.7	108	38.0	97.4	51.5	75.8	102	99.3	122	60.3	74.6	48.9	102	38.4	62.4	80.7

T a b l e 4

Comparison of the median (Md), minimal (Min), and maximal (Max) values for the content of analyzed elements in moss from Stobi with those for the whole territory of North Macedonia and six samples collected in the wider surroundings of Stobi

Element	Unit	Stobi (present study)		North Macedonia, 2015 (Stafilov et al., 2018)		The area around Stobi*, n = 6 (Stafilov et al., 2018)	
		Md	Min-Max	Md	Min-Max	Md	Min-Max
Ag	mg/kg	0.041	0.003–2.27	–	–	–	–
Al	%	0.56	0.28–5.22	0.21	0.070–0.74	0.21	0.13–0.37
As	mg/kg	0.31	0.16–0.98	0.54	0.13–1.4	0.72	0.46–1.11
B	mg/kg	6.71	0.39–27.4	–	–	–	–
Ba	mg/kg	41.0	21.6–197	42.0	9.7–180	50.5	36.4–85.3
Be	mg/kg	0.10	0.041–0.21	–	–	–	–
Bi	mg/kg	0.11	0.057–4.23	–	–	–	–
Ca	%	0.13	0.044–0.70	0.69	0.35–1.30	0.87	0.58–0.97
Cd	mg/kg	0.69	0.11–1.12	0.23	0.018–0.88	0.22	0.02–0.67
Co	mg/kg	5.47	2.19–12.7	0.60	0.16–2.0	0.97	0.64–2.01
Cr	mg/kg	43.1	17.3–124	5.7	1.8–31	13.9	10.7–31.5
Cu	mg/kg	11.6	6.60–27.4	4.6	3.0–8.3	3.62	3.47–8.28
Fe	%	0.66	0.33–1.19	0.17	0.051–0.46	0.25	0.16–0.37
Ga	mg/kg	1.34	0.66–3.89	–	–	–	–
Ge	mg/kg	1.08	0.56–2.05	–	–	–	–
K	%	0.32	0.10–0.48	0.60	0.31–1.40	0.59	0.50–0.76
Li	mg/kg	5.16	2.22–10.6	0.79	0.32–3.5	0.95	0.53–1.62
Mg	%	0.38	0.17–0.80	0.19	0.12–0.38	0.25	0.18–0.35
Mn	mg/kg	207	103–408	160	33–510	94.0	47.4–270
Mo	mg/kg	0.09	0.012–0.21	0.17	0.085–0.51	0.33	0.18–0.51
Na	mg/kg	152	72.7–282	190	140–380	185	158–246
Ni	mg/kg	103	54.4–300	3.5	0.68–63	20.9	7.60–63.3
P	mg/kg	285	77.7–582	–	–	–	–
Pb	mg/kg	22.3	10.2–58.0	4.9	2.2–14	4.70	3.50–7.92
Pd	mg/kg	0.014	0.008–0.03	–	–	–	–
S	mg/kg	1429	1048–1975	–	–	–	–
Sb	mg/kg	0.052	0.005–0.12	–	–	–	–
Se	mg/kg	0.039	0.022–0.08	–	–	–	–
Sn	mg/kg	0.506	0.14–0.95	–	–	–	–
Sr	mg/kg	49.7	19.0–155	25	6.5–220	52.8	26.6–59.7
Ti	mg/kg	7.54	2.09–28.6	–	–	–	–
Tl	mg/kg	0.063	0.014–0.29	–	–	–	–
V	mg/kg	0.23	0.091–0.48	3.3	0.47–11	4.81	3.76–6.17
Zn	mg/kg	70.7	38.0–122	30	12–66	42.8	32.5–46.8

*Near the villages of Otovica, Marena, Vataša, Bojančište, Pepelište and Lozovo. Md – median. Min – minimal value, Max – maximal value

This could be confirmed also from the data for the median and the range of the content of these elements in the six moss samples collected from the wider vicinity of Stobi. Namely, a noticeable increase in the median values of Ca, Co, Cr, Fe, Ni, and Zn in these samples compared to the median for the samples taken from the entire territory of North Macedonia (Table 5): the median content for Ca is 0.87% ranging from 0.58 to 0.97%, for Co is 0.97 mg/kg ranging from 0.64 to 2.01 mg/kg, for Cr is 13.9 mg/kg ranging from 10.7 to 31.5 mg/kg, for Cu is 3.62 mg/kg ranging from 3.47 to 8.28 mg/kg, for Fe is 0.25% ranging from 0.16 to 0.37%, for Ni is 20.9 mg/kg ranging from 7.6 to 63.3 mg/kg, for Pb is 4.7 mg/kg ranging from 3.5 to 7.92 mg/kg, and for Zn is 42.8 mg/kg ranging from 32.5 to 46.8 mg/kg.

This confirms the fact that the contamination of the moss samples from Stobi, apart from the substrate from which they were taken, also contributes to the distribution of dust from the surrounding soils, which, in turn, contain the elements with increased contents significantly more than the average for soils from the entire territory of North Macedonia. This is visible from the data shown in Table 4, where a comparison of the median, minimal and maximal values for the content of analyzed elements in soil samples from the whole territory of North Macedonia and four soil samples collected in the Stobi area is given. Of the elements whose content is particularly increased in the surrounding soils concerning their content in the soils of the entire territory of N. Macedonia's calcium stands out calcium (the ratio of the median content of 2.17), chromium (median ratio of 2.15), and nickel (median ratio of 2.22). According to the findings during the preparation of the Geochemical Atlas of the Republic of North Macedonia (Stafilov and Šajn, 2016), it was determined that the high content of these elements are found in soil over Neogene, Paleogene, and Mesozoic clastites, but their main source is weathering of Mesozoic ophiolites and ultrabasic magmatic rocks, demonstrated in the Republic of North Macedonia and other Balkan countries (Stafilov et al., 2010; Alijagić & Šajn, 2011; Šajn et al., 2013; Aliu et al., 2021). Due to weathering processes, the contents of Cr and Ni significantly increase in clastic sediments such as the Neogene, Paleogene, and Mesozoic clastitic rocks. The anomaly with increased contents is linked to the sediments along the Vardar river, the Vardar zone. It is one of the most expressed geochemical trends in the Republic of North Macedonia.

T a b l e 5

Comparison of the median, minimal and maximal values for the content of analyzed elements in soil samples from the whole territory of North Macedonia and four soil samples collected in the Stobi area

Element	Unit	North Macedonia (Stafilov and Šajn, 2016)			Four sampling locations around Stobi (Stafilov and Šajn, 2016)*			Median ratio
		Median	Minimum	Maximum	Median	Minimum	Maximum	Stobi/NM
Al	%	6.6	0.090	11	5.40	4.37	5.56	0.82
As	mg/kg	10	<1.0	720	8.50	8.00	10.0	0.85
Ba	mg/kg	430	6.0	2900	385	371	437	0.90
Be	mg/kg	2.0	<1.0	8.0	1.0	1.0	2.0	0.50
Bi	mg/kg	0.30	<0.10	15	0.20	0.20	0.30	0.67
Ca	%	1.3	0.050	35	2.82	2.05	6.54	**2.17**
Cd	mg/kg	0.30	<0.10	110	0.45	0.30	0.50	1.50
Co	mg/kg	17	0.50	150	15.9	14.2	17.2	0.94
Cr	mg/kg	88	5.0	2700	189	146	208	**2.15**
Cu	mg/kg	28	1.6	270	22.3	21.6	23.8	0.80
Fe	%	3.5	0.03	12	2.70	2.46	2.86	0.77
K	%	1.9	0.02	5.3	1.59	1.28	1.73	0.84
Li	mg/kg	26	1.8	210	23.1	22.1	26.8	0.89
Mg	%	0.94	0.12	13	1.035	0.85	1.36	**1.10**
Mn	mg/kg	900	17	>10000	749	694	807	0.83
Mo	mg/kg	0.90	<0.10	51	0.65	0.30	1.30	0.72
Na	%	1.2	0.013	6.0	1.13	0.94	1.31	0.94
Ni	mg/kg	46	2.1	2500	102	86.1	114	**2.22**
P	%	0.062	0.011	0.39	0.05	0.046	0.054	0.81
Pb	mg/kg	32	1.2	>10000	28.3	25	31.3	0.88
Sb	mg/kg	0.80	<0.10	630	0.85	0.70	1.00	1.06
Sn	mg/kg	2.6	<0.10	680	1.70	1.5	2.1	0.65
Sr	mg/kg	140	21	1400	181	146	264	**1.29**
Ti	mg/kg	0.34	0.004	1.2	0.30	0.28	0.33	0.88
Tl	mg/kg	0.70	<0.50	16	0.38	0.25	0.6	0.54
U	mg/kg	2.0	<0.10	13	1.40	1.2	1.6	0.70
V	mg/kg	89	<1.0	470	72.5	63	79	0.81
Zn	mg/kg	83	8.0	>10000	84	63	103	1.01

*Near the villages of Gradsko (2 samples), Palikura and Ulanci

This can be further confirmed by the calculated enrichment factors for the major anthropogenic elements in the moss and the soil samples collected in the vicinity of the Stobi site. Therefore, the enrichment factor (EF) was used to distinguish between the soil and/or airborne origin of trace elements in current moss. EF was calculated by using Al as a marker of soil substrate contamination of the moss samples (Frontasyeva and Pavlov, 2000; Sardans and Peñuelas, 2005):

$$\mathrm{EF} = \frac{w(M)_{moss//}/w(Al)_{moss}}{w(Al)_{soil}/w(Al)_{soil}},$$

where $w(M)$ represents the content of an individual major anthropogenic metallic pollutant (Cd, Co, Cr, Cu, Ni, and Pb) in current moss samples from the Stobi area and the substrate soil collected in the vicinity of the Stobi location. EF values higher than 1 represent the anthropogenic origin, and values higher than 3 represent remarkable airborne enrichment of the elements in moss samples (Sardans and Peñuelas, 2005). The obtained values for EF (Table 6) clearly show the significant influence on the cotamination of the moss samples with these elements from the surrounding soil substrate.

T a b l e 6

Values of the enrichment factors (EF) for the major anthropogenic metallic pollutants

Element	EF
Cd	14.8
Co	3.32
Cr	2.20
Cu	5.02
Ni	9.74
Pb	7.60

CONCLUSION

From the results of the analysis of the content of 33 elements (Ag, Al, As, B, Ba, Be, Bi, Ca, Cd, Co, Cr, Cu, Fe, Ga, Ge, K, Li, Mg, Mn, Mo, Na, Ni, P, Pb, Pd, S, Sb, Se, Sn, Sr, Ti, V, and Zn) in moss samples collected from 20 different locations in the ancient town of Stobi, North Macedonia, it could be concluded that the content of macroelements (Al, Fe, K, Mg) and for some microelements (Co, Cr, Cu, Ni, Pb, and Zn) in moss samples from the Stobi site are higher to those obtained for the moss samples collected from the whole territory of North Macedonia. This significant increase in the contents of these elements is especially noticeable in the samples of moss taken from the monuments in Stobi, whose substrate is the mortar between lime and sandstones or sandstone, and in some cases when the substrate is a marble. By the comparison of these data with those for the content of these elements in the six moss samples collected from the wider vicinity of Stobi it was also found the increased values for Ca, Co, Cr, Fe, Ni, Sr, V, and Zn, compared to the median for the samples taken from the entire territory of North Macedonia. This indicates the fact that the contamination of the moss samples from Stobi, apart from the substrate from which they were taken, is also affected by the dust from the surrounding soils, in which the content of elements with increased contents is significantly higher than the average for soils from the entire territory of North Macedonia.

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Р е з и м е

БИОМОНИТОРИНГ СО МОВ НА ЗАГАДУВАЊЕТО НА ВОЗДУХОТ И ПРОЦЕНА НА ЕФЕКТИТЕ ВРЗ АРХЕОЛОШКИТЕ ОБЈЕКТИ ВО СТОБИ, СЕВЕРНА МАКЕДОНИЈА

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Клучни зборови: загадување на воздухот; биомониторинг со мов; Стоби; Северна Македонија

Извршено е определување на содржината на 33 елементи (Ag, Al, As, B, Ba, Be, Bi, Ca, Cd, Co, Cr, Cu, Fe, Ga, Ge, K, Li, Mg, Mn, Mo, Na, Ni, P, Pb, Pd, S, Sb, Se, Sn, Sr, Ti, V и Zn) во примероци мов собрани од 20 различни локации во античкиот град Стоби, Северна Македонија. Определувањето е извршено со примена на индуктивно спрегната плазма со масена спектрометрија (ICP-MS) по извршена микробранова дигестија на примероците. Утврдено е дека вредностите на медијаната на содржината на макроелементите (Al, Ca, Fe, K, Mg), како и за некои специфични елементи во траги (Co, Cr, Cu, Ni, Pb и Zn) во примероците на мов од локалитетот Стоби се повисоки од оние добиени за примероците мов собрани од целата територија на Северна Македонија. Ваквото значително зголемување на содржината на овие елементи е посебно забележително кај примероците мов земени од спомениците во Стоби, чиј супстрат е малтерот помеѓу вар и песочници или песочник, а во некои случаи и кога подлогата е мермер. Сличен однос е забележан и кај податоците за медијаната и опсегот на содржината на овие елементи во шесте примероци мов собрани од поширокатa околина на Стоби, кои имаат забележително зголемување на вредностите на медијаната на Ca, Co, Cr, Fe, Ni, Sr и Zn споредено со медијаната за примероците земени од целата територија на С. Македонија. Констатирано е дека на контаминацијата на примероците мов од Стоби, освен подлогата од која се земени, влијае и распространетоста на правот од околните почви, во кои содржината на елементи со зголемена содржина е значително повисока од просекот за почвите од целата територија на Северна Македонија.