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# Atmospheric deposition of trace elements in Greece using moss *Hypnum cupressiforme* Hedw. as biomonitors

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#### Abstract

Mosses have been used for monitoring trace elements airborne pollution due to their ability to accumulate elements directly from wet and dry deposition. During the 2015/2016 European moss survey, ninety-five samples of *Hypnum cupressiforme* Hedw. were collected in Northern Greece. Mosses were analyzed to the content of Neutron Activation Analysis and the concentrations of thirty-three elements were determined. The contamination factors for the following elements Al, As, V, Ni, Fe, Cr, Zn were calculated. Information about air quality was provided through the study of atmospheric deposition of trace elements in mosses in the vicinity of Northern Greece.

Keywords Atmospheric deposition · Trace elements · Moss · Neutron activation analysis · Groundwater

# Introduction

Human activities have a great impact on atmospheric chemistry. Since industrial revolution and due to the increasing anthropogenic activities and urbanization, a lot of changes in atmosphere have occurred [1, 2]. Heavy metals can enter in all ecosystems while they are emitted to the atmosphere in different forms gas or particulate matter [3, 4]. There are different sources of the atmospheric emitted heavy metals

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such as housing and commercial properties, industrial processes, road transportations and agriculture. Heavy metals can be transported over long distances and be deposited many kilometers away from their emitting sources, impacting on human health and the environment [5]. Depending on their concentrations, they can be hazardous for plants, animals and humans affecting the whole food chain. The increase of atmospheric pollutants in urban and industrial areas and their influence in human health and environment represents one of the main European scientific concerns since the 1970's [2, 6]. As a result, controlling the air quality is considered necessary.

During the last 20 years, different instructions (1999/30/ EC, 2002/3/EC, 2004/107/EC and 2008/50/EC) have been officially followed by European community for air quality assessments related to metals, nitrogen oxides and dioxides, Sulphur dioxide, and ozone concentrations in the atmosphere [6]. The international cooperation for the reduction of air pollution during this period, has significantly contributed to the decrease of trace elements emissions in Europe [5, 7]. For monitoring the quality of air, different complementary modelling techniques are used, and they are mostly based on physico-chemical measurements of different air pollutants [8, 9]. Monitoring the quality of ambient air is a complex procedure, as it requires expensive analytic instrumentations, large number of potentially dangerous substances and temporal and spatial variations in the input rates of different pollutants [2, 9–11]. Beyond all the previous, the conventional methods that are used for the atmospheric deposition of heavy metals, require a big number of samples in frequent intervals, so the under investigation area can be pretty limited [4, 12–14]. Due to these difficulties, different alternatives were under investigation and finally the idea of biomonitoring became a reality in the late 1960's.

Biomonitoring is a technique that gives the possibility to detect spatial and temporal variations in the atmospheric deposition of different pollutants and to define their possible sources [2, 9, 15-25]. This technique uses living organisms as biomonitors either passively or actively, based on their sensitivity to air pollution or their capacity of accumulating pollutants in their tissues [2, 26, 27]. During the recent decades and among the different living organisms (vascular plants, mosses and lichens) that can be used as bioaccumulators of airborne pollutants [2, 28-31], mosses and lichens have been systematically chosen for environmental monitoring. Mosses are special living organisms- one of the earliest land plants in evolutionary terms [32], and they have reasonably attracted the interest of the researchers as they present very unique characteristics that are not noted in the other plants [33].

Using mosses as bioindicators of atmospheric fallout, is based on the fact that elemental concentrations in mosses are closely related to atmospheric deposition [34-38]. Mosses are able to accumulate airborne pollutants such as heavy metals [19, 35, 37, 39–42] and organic compounds [25] due to their morphological and physiological characteristics [2]. Mosses are non-vascular plants and they develop rhizoids while being in close contact to their substrate [43, 44]. They have no rooting system and all the nutrients and the water are obtained mainly from precipitation and dry deposition. The uptake of trace elements from the ground is not significant [22]. Due to their slow growth rate they are able to accumulate trace elements over a large time period. Each annual growth segment of mosses reveals the elemental concentrations of each current year [45]. Some moss species are appropriate for assessing the quality of air on large geographic scale due to the fact that they compose extensive populations [2, 20-24]. The concentrations of elements in mosses in a large geographic scale may vary because the accumulation of elements in moss tissues can be seriously influenced by local pollution sources and different environmental factors [2, 11, 19]. The moss analysis technique is an easy and less expensive method than the conventional deposition analysis as no special deposition collectors are required and a high sampling density can be carried out [22, 46, 47]. Mosses do not provide direct quantitative measurements of elements deposition in mosses. However, relating the information from different moss surveys to deposition monitoring data for each country, information about elemental concentrations can be extracted [22, 48, 49].

More specifically, the measured concentrations of elements in mosses and in wet deposition can be compared by using linear regression analysis. Then the elemental moss concentrations can be transformed to absolute deposition rates by using the calculated regression equations [48].

Since 1990 the European moss survey takes place every 5 years providing data for trace elements depositions from the atmosphere to naturally growing mosses [5, 7, 20, 22, 25, 50–55]. This European survey is being coordinated by the ICP Vegetation (International Cooperative Program on Effects of Air Pollution on Natural Vegetation and Crops) Coordination Centre at the Centre for Ecology and Hydrology, Bangor, UK [22]. Moss surveys provide spatial and temporal trends in trace elements concentration and the identification of local or transboundary sources [56, 57]. Greece provides for the first time data on concentrations of several moss monitored metals for the North part of the country. Hypnum cupressiforme is the most frequently moss species that can be found in the territory of Greece, due to the dry climate and the mountainous morphology in the biggest part of the country.

The objective of this study is to present the spatial atmospheric deposition of trace elements in the province of Northern Greece for identification of possible sources, as well as the comparison of the obtained results with the results of the neighboring and other European countries and set up the first database of the country for future surveys.

# Experimental

#### Study area and moss sampling

The study area was situated in the region of Northern Greece (Fig. 1). The sampling net included 95 sites in the Hellenic prefectures of West, Central, East Macedonia and Thrace, where the recommended moss species (*Hypnum Cupressiforme* Hedw., *Pseudoscleropodium purum*) could have been found in required quantities. More specifically sampling sites were located from 39.97° North to 41.65° North and from 20.97° East to 26.26° East covering a grid of 30 m  $\times$  30 m. Moss samples were collected from different elevations from 30 m to 1450 m above the mean sea level.

All samples of fresh plant material were collected during the end of summer 2016. There was no rain during the sampling. Samples were taken from open regions in most of the sampling sites avoiding possible contact of mosses with surface water. The sampling sites were located at least 300 m from main roads, 100 m from local roads and 200 m from populated areas. All samples were collected according to the requirements of the Protocol of the European Survey ICP Vegetation [50].



Fig. 1 Moss sampling net in 95 sites along the study area of Northern Greece

#### Sample preparation and analysis

All the samples were analyzed by means of Neutron Activation Analysis (NAA) performed in the radio-analytical Frank Laboratory of Neutron Physics, Joint Institute for Nuclear Research (JINR) in Dubna, Russia.

After sampling and identification of the moss species, mosses were cleaned from impurities very carefully and were stored in deep frozen until further treatment. No chemical treatment was used and mosses were not washed. Before analysis mosses were air-dried at 40 °C for 3 h. After that, the dried material was well homogenized on an agate mortar. From the homogenized material samples with weight of 0.3 g were measured on a scale and formed into the shape of pills by means of a pneumatic press and ceramic matrices. The pills were then packed in two separate ways—in plastic bags for short irradiation and in aluminum foil cups for long term irradiation.

Using a pneumatic rabbit system, the prepared and packed samples were sent to two different irradiation channels of the pulsed fast IBR-2 reactor of the JINR for long and short term irradiation respectively. The plastic packed samples were irradiated for 180 s to determine the short lived isotopes (Na, Mg, Al, Cl, Ti, V, Mn, Ni, I, In, Ag), while the aluminum packed samples were irradiated for 4–5 days to determine long lived isotopes (K, Ca, Sc, Cr, Fe, Co, Zn, As, Se, Br, Rb, Sr, Zr, Mo, Sb, Ba, La, Sm, Gd, Au, Th, U). The irradiated samples were then measured on HPGe detectors with relative efficiency 40% and 1.74 keV FWHM at the 1332 keV line of <sup>60</sup>Co. To determine the short lived isotopes, samples that were irradiated for a short period,

were measured immediately for 15 min. For the determination of long lived isotopes, samples that were irradiated for a long term, were measured once 3 days after the irradiation for 5 h, and then a second time, 20 days after the irradiation for 20 h. For the analysis of the gamma spectra the Genie-2000 software by Canberra was used. The elemental concentrations were calculated by means of a special software that was developed in FLNP, JINR [58]. Certified reference materials were used for the calculation of the elemental concentrations.

High quality certified reference materials (SRM) were used for the quality control of the NAA results, such as peach leaves-1547, coal fly ash-1633b and 1633c, coal-1632c, Montana soil-2710, San Joaquin Soil-2709 and Calcareous soil-ERM-CC690. All the reference materials were provided by the National Institute of Standards & Technology (NIST) and the Institute for Reference Materials and Measurements (ERM). The SRMs were packed and irradiated together with the moss samples under the same conditions in each transport container. The results that were obtained were compared with the certified values. The reference material that presented the least deviation between the measured and the certified values of each elemental concentration was chosen.

# **Results and discussion**

The concentrations of thirty-three elements were determined using the NAA. The results of the descriptive statistical analysis of the elemental concentrations in moss samples (mean, median, min, max, and standard deviation) are presented in Table 1. Spatial distributions of elemental concentrations (Fe, Ni, As, Zn, Cr) are shown in Figs. 2, 3, 4, 5 and 6.

This is the first attempt of studying the atmospheric deposition of trace elements in mosses, in such a big territory in Greece. Some years earlier, in Athens, close to a highly polluted area, moss bags were used for investigating the elemental atmospheric deposition [59]. According to this previous study, the concentrations of the elements Al, Zn, Fe, Cr, Ni, V were higher in the sites that were closer to the industrial zone, but there was not clear association between the anthropogenic activities and the observed elements.

Furtheremore, there was one study of biomonitoring, concerning the transboundary transport of trace elements between Bulgaria and the Northeastern part of Greece [57]. According to this study [57], in the Greek territory, the relative high concentrations of the elements As, Cr, Fe, Ni and V were due to old mines, soil contamination by windblown dust and road transportation. The same study showed that, the Pb–Zn complex close to Kardzahali town (Bulgaria) was responsible for the rise of the concentrations of Cr, Fe, Ni and As in the territory of Bulgaria.

The current study verifies the results of the previous investigation regarding the pollutants' chemical composition in the region of Northeastern part of Greece, next to the Bulgarian borders. Regions that are characterized by high concentrations of Al, As, Fe and V are observed in both of the studies, with some differences concerning the concentration levels of each element. More specifically, the concentration of As close to 'Kerkini Lake', presents a reduction of almost 30% from the previous study, while Al remains in similar levels. In specific regions close to Bulgarian boarders, the concentrations of Zn, Cr, Fe, Ni and V are two to three times higher than the previous observed concentrations. The reasons of this rise, ten years after the previous study, can be partially clarified. It might be due to the windblown dust coming from manufacturing and metals industries (Fe and Zn), or from coal mining activities and even from the ophiolitic rocks (Cr and Ni) that are present in the Greek territory. However, it might be due to transboundary transport from sources in Bulgarian boarders and further investigation needs to be done.

Moreover, in the areas that are close to the borders with F.Y.R. Macedonia, the elements Fe, V, Zn, As, Co, Ni and Cr show lower concentrations than in the Kavadarci region [56, 60] of F.Y.R. Macedonia, which is known for the ferronickel mining and other metallurgical activities. These concentrations verify the correlation of the above elements with the ferronickel mining, and maybe indicate a possible transboundary transfer of elements from F.Y.R. Macedonia to the Greek territory.

Differences can be observed between the elemental concentrations of the current data and the data of the other countries that participated in the 2005/2006 and 2010/2011

Table 1	Thec	concen	utration.	ns of	trace (	elemeni	ts in n	S SSOL	ample	s in (J	ີ ລຸ	) colle	cted	in No	rthern	Greed	ce det	ermin	ied us	ng N	eutron	Activ	ation	Analy	sis (N	AA)						
Element N	a N	Ag .	AI	D	X	Ca	Sc	Ë	>	L L	Mn	e	Ce	17	Zu Zu	As	Se B	r.	2	2	Zr	Mo A	5	S	-	Ba	La	Sm	Gd	Au	Ę	n
mean 1	730	4432	7886	5 145	6360	068 C	3 2.12	440	10.08	24.05	269	5974	3.02	12.83	56.56	2.45	0.23	6.48	21.59	52.13	35.18	0.28 0.	0.1 0.	0.59 0.	27 2.6	4 104	.7 5.42	0.237	0.44	0.001	2.07	0.55
StDev	232	289	669	Г (	305	3 332	2 0.19	34	0.63	3.65	20	532	0.33	1.31	5.41	0.31	0.01	0.30	1.76	3.91	3.99	0.03 0.	002 0	005 0.	04 0.1	2 9	.7 0.55	0.051	0.04	2E-04	. 0.25	0.06
median	751	3600	5840	130	567(	0 817C	0 1.44	327	8.17	11.50	219	3770	1.69	7.26	37.60	1.44	0.23	5.85	15.50	38.20	21.50	0.23 0.	055 0	004 0.	20 2.3	0 65	.9 3.22	0.008	0.32	7E-04	. 0.99	0.30
min	184	705	1350	) 47	216(	0 3960	0.29	76	2.61	2.04	34	1010	0.43	1.72	14.60	0.52	0.02	1.69	5.11	12.70	3.29	0.02 0	018 0	011 0.	02 1.0	3 15	.9 0.50	0.003	0.07	4E-05	0.28	0.07
max 5	210	17,800	46,100	380	17,200	0 23,400	3 8.92	1760	33.40	222	1090	28,700	20.3	90.20	282.0	17.90	0.48	15.00	82.9	197.0	219.0	2.31 0	16 0	233 3.	23 7.3	6 519	35.2	2 3.680	3.23	0.017	13.6	3.38



Fig. 2 Concentrations of As in  $(\mu g g^{-1})$  in moss samples in Northern Greece



Fig. 3 Concentrations of Cr in  $(\mu g \ g^{-1})$  in moss samples in the area of Northern Greece

moss surveys (Table 2) [25, 50]. More specifically, data from countries that are close to the vicinity of Greece, as well as far from Greece were chosen to be compared with the data of the current study. Greece presents lower maximum concentrations of Zn, Mn, Co than Norway, in contrast to the max elemental concentrations of Bulgaria and Switzerland. Ni max concentrations are almost in the same levels like in Bulgaria, but lower than in Norway and Albania. The Greek median value of As is similar to the Serbian one, but higher than F.Y.R. Macedonia and Albania. V and Zn are in the same levels in the Greek, Serbian and Croatian territory according to the 2005/2006 moss survey results.

In this study, there are evidence that elevated concentrations of trace elements are both observed in groundwater and mosses. More specifically, elevated concentration of Cr was observed in mosses as well as in groundwater in the central Macedonia, nearby the Anthemountas basin [71]. In Sarigiol basin, it has been reported the contribution of



Fig. 4 Concentrations of Fe in  $(\mu g g^{-1})$  in moss samples in the North part of Greece



Fig. 5 Concentrations of Ni in ( $\mu g g^{-1}$ ) in moss samples in Northern Greece

dispersed fly ash from the coal consumption to the pollution of groundwater [72] and soils and sediments [73], while Cr and Ni in mosses could also origin form the ophiolitic rocks in the study area. In literature, few studies have investigated linking between groundwater and mosses. Štechová et al. [74] studied the relationship of *Hamatocaulis vernicosus* with groundwater quality in Czech. Molchanov [75] studied the Gas exchange in sphagnum mosses nearby shallow groundwater. There is no direct transfer of elements from the groundwater to mosses, as the last ones do not have roots, and all the nutrients and water they need come from wet and dry deposition. Trace elements in groundwater are linked mainly with the geological background. Trace elements in mosses are linked mainly with their concentrations in air. Elevated concentrations of trace elements in both mosses and in groundwater might be an indicator of pollution transfer from the air to mosses as well as from the air



Fig. 6 Concentrations of Zn in ( $\mu g g^{-1}$ ) in moss samples in the region of Northern Greece

**Table 2** The concentrations of seven trace elements (As, Cr, Fe, Ni, V, Zn, Al) in moss samples (mg kg<sup>1</sup>) from the current survey and from otherEuropean countries derived from the 2005/2006 and 2010/2011 moss survey

As Median ( <i>min–max</i> )	Cr Median ( <i>min-max</i> )	Fe Median ( <i>min–max</i> )	Ni Median ( <i>min–max</i> )	V Median ( <i>min–max</i> )	Zn Median ( <i>min–max</i> )	Al Median ( <i>min–max</i> )	
1.44	11.5	3770	7.26	8.17	37.6	5840	Current study
(0.52–17.9)	(2.04–222)	(1010-28,700)	(1.72–90.2)	(2.61–33.4)	(14.6–282)	(1350-46,100)	
-	2.43	1399	2.99	3.88	27.9	1495	Bulgaria, 2005
-	(0.79–57.8)	(186–9493)	(0.92–90)	(0.77–24.3)	(9.38–366)	(426–10,394)	[61]
0.63	2.06	1101	2.61	3.07	22.2	1245	Bulgaria, 2010
(0.15–10.8)	(0.72–38.1)	(307–8546)	(0.84-82.1)	(0.96–22.4)	(8.22–286)	(402-8886)	[25]
0.68	6.79	2239	5.82	6.38	35.6	3600	F.Y.R. Macedonia, 2005
(0.18–4.32)	(2.09-82)	(999–8130)	(1.8–43.1)	(2.5–31.9)	(16.4–91.3)	(1466–25,860)	[62]
0.48	6.46	1900	4.3	3.8	29	2400	F.Y.R. Macedonia, 2010
(0.23–1.9)	(2.46–35)	(890–5400)	(1–55)	(1.5–14)	(13–94)	(1100–6800)	[63]
0.12	0.58	273	1.24	1.40	31.4	255	Norway, 2005
(0.004–4.61)	(0.099–65.5)	(50.4–9972)	(0.055–1016)	(0.25–22.1)	(8.04–694)	(58.3–12,121)	[64]
0.13	0.59	278	1.16	1.41	30.7	283	Norway, 2010
(0.02–4.84)	(0.16–47.9)	(27–24,684)	(0.15-857)	(0.29–25.9)	(7.4–368)	(46–4581)	[65]
1.41	6.44	2267	4.43	5.76	29.0	3946	Serbia, 2005
(0.22–21.6)	(2-78.8)	(670–16,100)	(1.7–23.8)	(1.94–32.7)	(13.2–259)	(117–31,180)	[66]
0.305	4.75	1618	5.85	3.51	13.8	1638	Albania, 2010
(0.05–2.86)	(1.62–31.8)	(469–5488)	(1.56–131)	(1.15–16.9)	(1-68.1)	(535–6974)	[67, 68]
0.37	2.8	1000	2.7	3.1	29	1350	Croatia, 2005
(0.1–6)	(0.76–33)	(320–12,140)	(0.66–18)	(0.91–32)	(12–283)	(398–21,460)	[69]
0.36	1.94	789	3.16	2.55	24.8	878	Croatia, 2010
(0.05–1)	(0.41-8.55)	(85–4028)	(1.04–14.66)	(0.23–37.3)	(11.6–77.1)	(112–4493)	[70]
0.15	1.2	261	1.59	0.67	31.4	-	Switzerland, 2005
(0.053–1.07)	(0.33–7.96)	(95.4–2380)	(0.5 - 7.77)	(0.21–3.55)	(10.1–179)	-	[61]

through soil to groundwater. Obviously, the trace elements concentrations in mosses should be compared with nearby soil concentrations, linked with the geological formations. The aforementioned constitutes the next step of this study.

Another method for identifying the most affected areas by the atmospheric deposition of elements is the calculation of the contamination factor. The contamination factor shows the pollution status of the under study area [76–81]. The contamination factors (CF) for each sampling site for the elements Al, As, Fe, Ni, V, Cr, Zn were calculated according to the following formula (Eq. 1).

$$CF = \frac{Concentration of element (\mu g g^{-1})}{Background level concentration (\mu g g^{-1})}$$
(1)

where the background level is considered to be the concentration of each element in a "clean- virgin" area in the territory of Greece, which is as less as possible affected by human activities and other local sources, such as metal industry, mining and agricultural activities, oil combustion and road transportation.

The dispersion of contaminants in the atmosphere can occur independently of the media or the organisms on which they are deposited [68–70]. Considering this, there are different contamination factor scales [77, 82] and each area can be characterized by different contamination levels, according to the calculated CF values. According to Mouvet [83], who had studied the elemental concentrations in aquatic mosses, areas with CF < 2 can be considered non polluted due to the natural variability that can be found into an ecosystem.

There is another scale of classification of the CF, which was established by Fernández et al. [78] based on specific approaches in terrestrial mosses:

- CF < 1, it's a non-polluted area (natural origin of the element).
- 1 < CF < 2, it's a suspected area.
- 2 < CF < 3.5 is a slightly polluted area.
- 3.5 < CF < 8 it's a moderately polluted area.
- 8 < CF < 27 it's a serious polluted area.
- CF > 27 it's an extreme polluted area.

In the present study, more than 50% of the sampling sites have CF < 1, concerning the elements Al, As, V, Fe, Zn., while this percentage drops down to 30% concerning Cr and Ni elements. This indicates that most of the above elements in mosses in these regions are not affected by any anthropogenic factor but they have natural origin. Around 30% of the areas are considered suspected areas (1 < CF < 2) for almost all the elements, while less than 15% are characterized slightly polluted areas (2 < CF < 3.5). The rise of these elemental concentrations is probably due to human activities and other local sources. Around 5% of the areas, (except of Cr and Ni that are around 20%), are described moderately polluted areas (3.5 < CF < 8) indicating that human activities have even stronger impact on these sites. These regions are mostly in the prefecture of Central Macedonia. Finally, around 5% of the regions (mostly those in the prefecture of West Macedonia)present high enough concentrations of Cr and Ni, in order to be marked as serious polluted areas (8 < CF < 27). The regions where Cr and Ni present high concentrations are in accordance with those regions whose CF > 1, indicating that they might be connected not only with ophiolitic rocks (geogenic source of origin) but also with human activities such as coal mining and industry.

The contamination factor was calculated in other studies too for the characterization of the areas. For example, Maxhumi et al. [84] mentions that in Kosovo the elements Fe, Ni and Zn are related with the first two categories of the contamination factor scale, indicating non polluted areas, while Cr is associated with the third and fourth level of contamination factor, the so called slightly and moderately polluted areas. According to Jiang et al. [81], in China, Cr is connected with regions that have experienced moderate contamination, while As, Ni, V and Zn characterize areas with low contamination level (first category of the CF scale). In Galicia (northwest Spain), according to Fernández and Carballeira [77], most of the areas concerning Al, Cr, Fe, Ni and Zn belong to the second category of CF, while there is a 2% of areas with serious contamination level associated with Al and Fe elements. In Albania, Qarri et al. [67] reported that Zn is correlated with the first two levels of CF scale, while As is characterizing areas that are slightly polluted. The CF of the elements Fe, Ni, V and Al describe areas that are moderately and serious polluted in Albanian territory.

# Conclusions

Moss biomonitoring is a really efficient and economical technique for the determination of the atmospheric deposition of trace elements. Ninety-five samples of mosses were collected from the vicinity of Northern Greece. They were analyzed using NAA and the concentrations of 33 elements were determined. A detailed spatial distribution of the elements was achieved.

The values of the present study were compared with the results of the previous EU moss surveys, and more precisely with those of the 2005/2006 and 2010/2011 moss survey. The regions with the higher concentrations of Al, As, Fe and V of this study are in accordance with the data of the previous study that was conducted in the same region by Yurukova et al. [57]. In specific sites close to Bulgarian boarders, the elements Zn, Cr, Fe, Ni and V are found in

higher concentrations than in the previous study. The reasons of this rise, has not be defined yet. It might be due to transboundary transport or due to local sources in the Greek territory. Further research should be done for the definition of the sources that lead to this rise.

The relative higher concentrations of Cr and Ni in the territory of Greece are probably due to geogenic sources (ophiolitic rocks), and maybe due to coal mining activities. Al, Fe and Zn might be connected with metal and manufacturing activities. Future investigation about the determination of potential sources of the studied elements in mosses is required. Also the case of transboundary transfer of metals should be examined more carefully.

Elevated concentrations of trace elements are coobserved in groundwater and mosses, indicating the pollution transfer from the air to mosses and from the air through soil to groundwater. The elemental concentrations in mosses should be compared with nearby soil concentrations, linked with the geological formations. A further and more detailed analysis is necessary to understand potential process between mosses and groundwater.

The contamination profile of each area is also formed using the contamination factor. The CF results indicate that the elements Al, As, Fe, V, Zn are associated with the first category of the contamination scale—the unpolluted areas, revealing a pretty low pollution level of atmospheric deposition of the above elements. The elements Cr and Ni are mostly related with the suspected areas—second category of the CF, emphasizing on the impact of human activities on their atmospheric deposition.

Finally, this study provides a baseline dataset for future studies, in order to evaluate the air quality of Greece and compare with data from other neighboring countries.

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### References

- 1. Seinfeld JH, Pandis SN (2006) Atmospheric chemistry and physics—from air pollution to climate change, 2nd edn. Wiley, Hoboken
- Gerdol R, Marchesini R, Iacumin P, Brancaleoni L (2014) Monitoring temporal trends of air pollution in an urban area using mosses and lichens as biomonitors. Chemosphere 108:388–395
- Herpin U, Berlekamp J, Markert B, Wolterbeek B, Grodzinska K, Siewers U, Lieth H, Weckert V (1996) The distribution of heavy metals in a transect of the three states the Netherlands, Germany and Poland, determined with the aid of moss monitoring. Sci Total Environ 187:185–198

- Cucu-Man S, Mocanu R, Culicov O, Steinnes E, Frontasyeva M (2004) Atmospheric deposition of metals in Romania studied by biomonitoring using the epiphytic moss *Hypnum cupressiforme*. Int J Environ Anal Chem 84(11):845–854
- Meyer C, Diaz-de-Quijano M, Monna F, Franchi M, Toussaint M, Gilbert D, Bernard N (2015) Characterization and distribution of deposited trace elements transported over long and intermediate distances in north-eastern France using *Sphagnum* peatlands as a sentinel ecosystem. Atmos Environ 101:286–293
- 6. Di Palma A, Crespo Pardo D, Spagnuolo V, Adamo P, Bargagli R, Cafasso D, Capozzi F, Aboal JR, González AG, Pokrovsky O, Beike AK, Reski R, Tretiach M, Varela Z, Giordano S (2016) Molecular and chemical characterization of a *Sphagnum palustre* clone: key steps towards a standardized and sustainable moss bag technique. Ecol Indicat 71:388–397
- Ilyin I, Rozovskaya O, Travnikov O, Varygina M, Aas W, Uggerud H T (2013) Heavy metals: transboundary pollution of the environment (No. Status Report 2/2013). EMEP/MSC-E/CCC/CEIP
- EU 2008. Directive 2008/50/EC of the European Parliament and of the Council of 21 May 2008 on ambient air quality and cleaner air for Europe. Off J 1–44. 11.062008, L152
- Adamo P, Giordano S, Sforza A, Bargagli R (2011) Implementation of airborne trace element monitoring with devitalized transplants of *Hypnum cupressiforme* Hedw.: assessment of temporal trends and element contribution by vehicular traffic in Naples city. Environ Pollut 159:1620–1628
- 10. Boubel RW, Fox DL, Turner DB, Stern AC (1994) Fundamentals of air pollution. Academic Press, San Diego
- Tørseth K, Aas W, Breivik K, Fjaraa AM, Fiebig M, Hjellbrekke AG, Lund Myhre C, Solberg S, Yttri KE (2012) Introduction to the European Monitoring and Evaluation Programme (EMEP) and observed atmospheric composition change during 1972–2009. Atmos Chem Phys 12:5447–5481
- 12. Maenhaut W (1989) Analytical techniques for atmospheric trace elements. In: Pacyna JM, Ottar B (eds) Control and fate of atmospheric trace metals. NATO ASI Series (Series C: Mathematical and Physical Sciences), vol 268. Springer, Dordrecht
- Wrinkel P, Schultz M, Dannecker W (1991) Problems with the determination of heavy metals in precipitation. Fresenius J Anal Chem 340:575. https://doi.org/10.1007/BF00322432
- Richter DAU, Williams WP (1998) Assessment and management of urban air quality in Europe. EEA Monograph 5, 141 pp. EEA, Copenhagen 1998
- Pott U, Turpin DH (1998) Assessment of atmospheric heavy metals by moss monitoring with *isothecium stoloniferum* brid. In the Fraser Valley B.C., Canada. Water Air Soil Pollut 101:25–44
- Bargagli R (1998) Trace elements in terrestrial plants. An ecophysiological approach to biomonitoring and biorecovery. Springer, Berlin, p 324
- Markert BA, Breure AM, Zechmeister HG (2003) Bioindicators and biomonitors: principles, concepts, and applications. Elsevier, Amsterdam
- Lehto J, Paatero J, Pehrman R, Kulmala S, Suksi J, Koivula T, Jaakkola T (2008) Deposition of gamma emitters from Chernobyl accident and their transfer in lichen–soil columns. J Environ Radioact 99:1656–1664
- Schröder W, Pesch R, Englert C, Harmens H, Suchara I, Zechmeister HG, Thöni L, Maňkovska B, Jeran Z, Grodzińska K, Alber R (2008) Metal accumulation in mosses across national boundaries: uncovering and ranking causes of spatial variation. Environ Pollut 151:377–388
- 20. Schröder W, Holy M, Pesch R, Harmens H, Ilyin I, Steinnes E, Alber R, Aleksiayenak Y, Blum O, Coşkun M, Dam M, De Temmerman L, Frolova M, Frontasyeva M, Gonzalez Miqueo L, Grodzińska K, Jeran Z, Korzekwa S, Krmar M, Kubin E, Kvietkus K, Leblond S, Liiv S, Magnusson SH, Maňkovska B,

Piispanen J, Rühling A, Santamaria JM, Špirić Z, Suchara I, Thöni L, Urumov V, Yurukova L, Zechmeister HG (2010) Are cadmium, lead and mercury concentrations in mosses across Europe primarily determined by atmospheric deposition of these metals? J Soils Sedim 10:1572–1584

- 21. Holy M, Pesch R, Schröder W, Harmens H, Ilyin I, Alber R, Aleksiayenak Y, Blum O, Coşkun M, Dam M, De Temmerman L, Fedorets N, Figueira R, Frolova M, Frontasyeva M, Goltsova N, Gonzalez Miqueo L, Grodzińska K, Jeran Z, Korzekwa S, Krmar M, Kubin E, Kvietkus K, Larsen M, Leblond S, Liiv S, Magnússon SH, Maňkovská B, Mocanu R, Piispanen J, Rühling A, Santamaria JM, Steinnes E, Suchara I, Thöni L, Turcsanyi G, Urumov V, Wolterbeek B, Yurukova L, Zechmeister HG (2009) First thorough identification of factors associated with Cd, Hg and Pb concentrations in mosses sampled in the European Surveys 1990, 1995, 2000 and 2005. J Atmos Chem 63:109–124
- 22. Harmens H, Norris DA, Steinnes E, Kubin E, Piispanen J, Alber R, Aleksiayenak Y, Blum O, Coşkun M, Dam M, De Temmerman L, Fernández JA, Frolova M, Frontasyeva M, Gonzalez-Miqueo L, Grodzińska K, Jeran Z, Korzekwa S, Krmar M, Kvietkus K, Leblond S, Liiv S, Magnusson SH, Maňkovska B, Pesch R, Rühling A, Santamaria JM, Schröder W, Spiric Z, Suchara I, Thöni L, Urumov V, Yurukova L, Zechmeister HG (2010) Mosses as biomonitors of atmospheric heavy metal deposition: spatial patterns and temporal trends in Europe. Environ Pollut 158:3144–3156
- 23. Harmens H, Norris DA, Cooper DM, Mills G, Steinnes E, Kubin E, Thöni L, Aboal JR, Alber R, Carballeira A, Coşkun M, De Temmerman L, Frolova M, Gonzalez-Miqueo L, Jeran Z, Leblond S, Liiv S, Maňkovská B, Pesch R, Poikolainen J, Rühling A, Santamaria Simonèiè P, Schröder W, Suchara I, Yurukova L, Zechmeister HG (2011) Nitrogen concentrations in mosses indicate the spatial distribution of atmospheric nitrogen deposition in Europe. Environ Pollut 159:2852–2860
- 24. Harmens H, Ilyin I, Mills G, Aboal JR, Alber R, Blum O, Coşkun M, De Temmerman L, Fernández JA, Figueira R, Frontasyeva M, Godzik B, Goltsova N, Jeran Z, Korzekwa S, Kubin E, Kvietkus K, Leblond S, Liiv S, Magnússon SH, Maňkovská B, Nikodemus O, Pesch R, Poikolainen J, Radnović D, Rühling A, Santamaria JM, Schroder W, Špirić Z, Stafilov T, Steinnes E, Suchara I, Tabors G, Thöni L, Turcsanyi G, Yurukova L, Zechmeister HG (2012) Country-specific correlations across Europe between modelled atmospheric cadmium and lead deposition and concentrations in mosses. Environ Pollut 166:1–9
- 25. Harmens H, Norris D A, Mills G, The Participants of the Moss Survey (2013) Heavy Metals and Nitrogen in Mosses: Spatial Patterns in 2010/2011 and Long-term Temporal Trends in Europe. ICP Vegetation Programme Coordination Centre, Centre for Ecology and Hydrology, Bangor, UK
- Falla J, Laval-Gilly P, Henryon M, Morlot D, Ferard JF (2000) Biological air quality monitoring: a review. Environ Monit Assess 64:627–644
- 27. Wolterbeek B (2002) Biomonitoring of trace element air pollution: principles, possibilities and perspectives. Environ Pollut 120:11–21
- Malizia D, Giuliano A, Ortaggi G, Masotti A (2012) Common plants as alternative analytical tools to monitor heavy metals in soil. Chem Cent J 6(Suppl. 2):S6. https://doi.org/10.1186/1752-153X-6-S2-S6
- Conti ME, Cecchetti G (2001) Biological monitoring: lichens as bioindicators of air pollution assessment – a review. Environ Pollut 114:471–492
- Onianwa PC (2001) Monitoring atmospheric metal pollution: a review of the use of mosses as indicators. Environ Monit Assess 71:13–50

- Paatero J, Jaakkola T, Kulmala S (1998) Lichen (sp. *Cladonia*) as a deposition indicator for transuranium elements investigated with the Chernobyl fallout. J Environ Radioact 38(2):223–247
- Decker EL, Frank W, Sarnighausen E, Reski R (2006) Moss systems biology en route: phytohormones in *Physcomitrella* development. Plant Biol 8:397–406. https://doi.org/10.1055/s-2006-92395
- Czarnowska K, Rejment-Grochowska I (1974) Concentration of heavy metals- iron, manganese, zinc and copper in mosses. Acta Soc Bot Pol XLIII(1):39–44
- 34. Little P, Martin MH (1974) Biological monitoring of heavy metal pollution. Environ Pollut 6:1–19
- 35. Rühling Å, Tyler G (1968) An ecological approach to the lead problem. Bot Notiser 121:321–342
- Gjengedal E, Steinnes E (1990) Uptake of metal ions in moss from artificial precipitation. Environ Monit Assess 14(1):77–87
- Tyler G (1990) Bryophytes and heavy-metals: a literature review. Bot J Linn Soc 104:231–253
- Steinnes E, Rambaek J, Hanssen E (1992) Large scale multi-element survey of atmospheric deposition using naturally growing moss as biomonitor. Chemos 25(5):735–752
- 39. Herrmann R (1976) Modellvorstellungen zur rauemlichen Verteilung von Spurenmetall-verunreinigungen in der Bundesrepublik Deutschland, angezeight durch den Metallgehalt in epiphytischen Moosen. Erdkunde (Sonderdruck), Archiv fuer wissenschaftliche Geographie, Band 30, Lfg. 4, Bonn
- 40. Tomassini FD, Puckett KJ, Nieboer E, Richardson DHS, Grace B (1976) Determination of copper, iron, nickel and sulphur by X-ray fluorescence in lichens from the Mackenzie Valley, Northwest Territories and the Sudbury district, Ontario. Can J Bot 54:1591–1603
- Thomas W (1986) Representativity of mosses as biomonitor organisms for the accumulation of environmental chemicals in plants and soils. Ecotoxicol Environ Saf 11:339–346
- Bargagli R, Brown DH, Nelli L (1995) Metal biomonitoting with mosses: procedures for correcting for soil contamination. Environ Pollut 89(2):169–175
- 43. Glime JM (2017) Bryophyte ecology. Volume 1. Physiological Ecology. Ebook sponsored by Michigan Technological University and the International Association of Bryologists. Last updated 25 March 2017 and available at http://digitalcommons.mtu.edu/bryop hyte-ecology/
- Schwartzenberg K (2006) Moss biology and phytohormones— Cytokinins in *Physcomitrella*. Plant Biol 8:382–388. https://doi. org/10.1055/s-2006-923962
- Chakrabortty S, Paratkar GT (2006) Biomoitoring of trace element air pollution using mosses. Aeros Air Qual Res 6(3):247–258
- 46. Berg T, Røyset O, Steinnes E (1995) Moss (*Hylocomium splend-ens* used as biomonitor of atmospheric trace element deposition: estimation of uptake efficiencies. Atmos Environ 29(3):353–360
- 47. Gusev A, Iliyn I, Rozovskaya O, Shatalov V, Sokovych V, Travnikov O (2009) Modelling of heavy metals and persistent organic pollutants: New developments. EMEP/MSC-E Technical Report 1/2009. Meteorological Synthesizing Centre e East, Moscow, Russian Federation. http://www.msceast.org
- Berg T, Steinnes E (1997) Use of mosses (*Hylocomium splendens* and *Pleurozium schreberi*) as biomonitors of heavy metal deposition: from relative to absolute values. Environ Pollut 98:61–71
- 49. Berg T, Hjellbrekke A, Rühling Å, Steinnes E, Kubin E, Larsen MM, Piispanen J (2003) Absolute deposition maps of heavy metals for the Nordic countries based on the moss survey. TemaNord 2003:505, Nordic Council of Ministers, Copenhagen, Denmark
- Harmens H, Norris DA, The Participants of the Moss Survey, (2008) Spatial and Temporal Trends in Heavy Metal Accumulation in Mosses in Europe (1990-2005). ICP Vegetation

Programme Coordination Centre, Centre for Ecology and Hydrology, Bangor, UK

- 51. Travnikov O, Ilyin I, Rozovskaya O, Varygina M, Aas W, Uggerud H T, Mareckova K, Wankmueller R (2012) Long-term Changes of Heavy Metal Transboundary Pollution of the Environment (1990–2010) (No. Status Report 2/2012). EMEP/MSC-E/CCC/ CEIP
- Travnikov O, Ilyin I (2005) Regional Model MSCE-HM of Heavy Metal Transboundary Air Pollution in Europe (Technical Report No. 6/2005). EMEP/MSC-E
- 53. Buse A, Norris D, Harmens H, Büker P, Ashenden T, Mills G (2003) Heavy metals in European mosses: 2000/2001 survey. ICP Vegetation Programme Coordination Centre, Centre for Ecology and Hydrology, Bangor, UK. http://icpvegetation.ceh.ac.uk
- Rühling Å (1994) Atmospheric heavy metal deposition in Europeestimation based on moss analysis. NORD 1994:9 Nordic Council of Ministers, Copenhagen, Denmark
- Rühling Å, Steinnes E (1998) Atmospheric heavy metal deposition in Europe 1995–1996. NORD 1998:15, Nordic Council of Ministers, Copenhagen, Denmark
- Barandovski L, Cekova M, Frontasyeva MV, Pavlov SS, Stafilov T, Steinnes E, Urumov V (2008) Atmospheric deposition of trace element pollutants in Macedonia studied by the moss biomonitoring technique. Environ Monit Assess 138:107–118
- Yurukova L, Tsakiri E, Çayir A (2009) Cross-border response of moss *Hypnum cupressiforme* Hedw., to atmospheric deposition in Southern Bulgaria and Northeastern Greece. Bull Environ Contam Toxicol 83:174–179. https://doi.org/10.1007/s00128-008-9601-8
- Dmitriev AY, Pavlov SS (2013) Automation of the quantitative determination of elemental content in samples using neutron activation analysis on the IBR-2 reactor at the frank laboratory for neutron physics, joint institute for nuclear research. Phys Part Nucl Lett 10(1):33–36. https://doi.org/10.1134/S1547477113010056
- Saitanis CJ, Frontasyeva MV, Steinnes E, Palmer MW, Ostrovnaya TM, Gundorina SF (2012) Spatiotemporal distribution of airborne elements monitored with the moss bags technique in the Greater Thriasion Plain, Attica, Greece. Environ Monit Assess. https:// doi.org/10.1007/s10661-012-2606-0
- Bačeva K, Stafilov T, Šajn R, Tănăselia C (2012) Moss biomonitoring of air pollution with heavy metals in the vicinity of a ferronickel smelter plant. J Environ Sci Health A 47:645–656
- Thöni L, Yurukova L, Bergamini A, Ilyin I, Matthaei D (2011) Temporal trends and spatial patterns of heavy metal concentrations in mosses in Bulgaria and Switzerland: 1990-2005. Atmos Environ 45:1899–1912
- Barandovski L, Frontasyeva MV, Stafilov T, Šajn R, Pavlov S, Enimiteva V (2012) Trends of atmospheric deposition of trace elements in Macedonia studied by the moss biomonitoring technique. J Environ Sci Health A 47(13):2000–2015
- Barandovski L, Frontasyeva MV, Stafilov SS, Šajn T, Ostrovnaya R (2015) Multi-element atmospheric deposition in Macedonia studied by the moss biomonitoring technique. Environ Sci Pollut Res 22:16077–16097. https://doi.org/10.1007/s11356-015-4787-x
- Steinnes E, Berg T, Uggerud H, Vadset M (2007) Atmospheric Deposition of Heavy Metals in Norway. Nation-wide survey in 2005, State Program for Pollution Monitoring, Report 980/2007. Norwegian State Pollution Control Authority, Oslo (in Norwegian)
- 65. Steinnes E, Berg T, Uggerud H T, Pfaffhuber K A (2011) Atmospheric deposition of heavy metals in Norway, National Study in 2010, Rapport 1109/2011. Norwegian University of Science and Technology, Trondheim (in Norwegian)
- 66. Frontasyeva MV, Ye Galinskaya T, Krmar M, Matavuly M, Pavlov SS, Povtoreyko EA, Radnovic D, Steinnes E (2004) Atmospheric deposition of heavy metals in northern Serbia and Bosnia-Herzegovina studied by the moss biomonitoring,

neutron activation analysis and GIS technology. J Radioanal Nucl Chem 259:141–147

- Qarri F, Lazo P, Stafilov T, Frontasyeva M, Harmens H, Bekteshi L, Baceva K, Goryainov Z (2014) Multi-elements atmospheric deposition in Albania. Environ Sci Pollut Res 21:2506–2518. https://doi.org/10.1007/s11356-013-2091-1
- Bekteshi L, Lazo P, Qarri F, Stafilov T (2015) Application of the normalization process in the survey of atmosphericdeposition of heavy metals in Albania through moss biomonitoring. Ecol Indic 56:50–59
- Špirić Z, Frontasyeva M, Steinnes E, Stafilov T (2012) Multielement atmospheric deposition study in Croatia. Int J Environ Anal Chem 92(10):1200–1214
- Špirić Z, Vučkovič I, Stafilov T, Kušan V, Frontasyeva M (2013) Air pollution study in croatia using moss biomonitoring and ICP–AES and AAS analytical techniques. Arch Environ Contam Toxicol 65:33–46. https://doi.org/10.1007/s00244-013-9884-6
- 71. Kazakis N, Kantiranis N, Voudouris KS, Mitrakas M, Kaprara E, Pavlou A (2015) Geogenic Cr oxidation on the surface of mafic minerals and the hydrogeological conditions influencing hexavalent chromium concentrations in groundwater. Sci Total Environ 514:224–238
- 72. Kazakis N, Kantiranis N, Kalaitzidou K, Kaprara E, Mitrakas M, Frei R, Vargemezis G, Tsourlos P, Zouboulis A, Filippidis A (2017) Origin of hexavalent chromium in groundwater: the example of Sarigkiol Basin, Northern Greece. Sci Total Environ 593–594:552–566
- 73. Kazakis N, Kantiranis N, Kalaitzidou K, Kaprara E, Mitrakas M, Frei R, Vargemezis G, Vogiatzis D, Zouboulis A, Filippidis A (2018) Environmentally available hexavalent chromium in soils and sediments impacted by dispersed fly ash in Sarigkiol basin (northern Greece). Environ Pollut 235:632–641
- 74. Štechová T, Holá E, Manukjanová A, Mikulášková E (2010) Distribution and habitat requirements of the moss *Hamatocaulis vernicosus* (Mitt.) Hedenäs in the Bohemian Forest. Silva Gabreta 16:1–11
- Molchanov AG (2015) Gas exchange in sphagnum mosses at different near-surface groundwater levels. Ekologiya 2015(3):182–188
- 76. Gonçalves EPR, Boaventura RAR, Mouvet C (1992) Sediments and aquatic mosses as pollution indicators for heavy metals in the Ave River basin (Portugal). Sci Tot Environ 114:7–24
- 77. Fernández JA, Carballeira A (2001) A comparison of indigenous mosses and topsoils for use in monitoring atmospheric heavy metal deposition in Galicia (northwest Spain). Environ Pollut 114:431–441
- Fernández JA, Aboal JR, Carballeira A (2000) Use of native and transplanted mosses as complementary techniques for biomonitoring mercury around an industrial facility. Sci Total Environ 256:151–161
- Fernandez JA, Rey A, Carballeira A (2000) An extended study of heavy metal deposition in Galicia (NW Spain) based on moss analysis. Sci Total Environ 254:31–44. https://doi.org/10.1016/ S0048-9697(00)00431-9
- Carballeira A, Couto JA, Fernández JA (2002) Estimation of background levels of various elements in terrestrial mosses from Galicia (NW Spain). Water Air Soil Pollut 133:235–252
- 81. Jiang Y, Fan M, Hu R, Zhao J, Wu Y (2018) Mosses are better than leaves of vascular plants in monitoring atmospheric heavy metal pollution in urban areas. Int J Environ Res Public Health 15:1105. https://doi.org/10.3390/ijerph15061105
- Fernández JA, Carballeira A (2000) Evaluation of contamination by different elements in terrestrial mosses. Arch Environ Contam Toxicol 40:461–468. https://doi.org/10.1007/s0024 40010198

- Mouvet C (1986) Metaux lourds et mousses aquatiques. Synthese methodologique. Report, Agence de l'Eau Rhone-Med.-Corse, Metz, 110
- 84. Maxhuni A, Lazo P, Kane S, Qarri F, Marku E, Harmens H (2016) First survey of atmospheric heavy metal deposition in Kosovo using moss biomonitoring. Environ Sci Pollut Res 23:744–755. https://doi.org/10.1007/s11356-015-5257-1

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