



Active biomonitoring of potentially toxic elements in urban air by two distinct moss species and two analytical techniques: a pan-Southeastern European study

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Abstract

This is the first study to use moss transplants as a biomonitoring technique and inductively plasma mass spectrometry to investigate airborne potentially toxic element pollution and air quality in urban areas on a regional scale across nine Southeastern European countries. The mosses in bags were exposed for 2 months during the winter season (2019/2020) at five sites in each of the selected urban areas next to air quality (AQ) monitoring stations. The sites were selected concerning different land use classes (typical urban, residential, urban background, and rural sites). The concentrations of 35 elements were determined using inductively coupled plasma mass spectrometry. A comparison with elemental analysis performed by total reflection X-ray fluorescence is also presented. Concentrations of the potentially toxic element in moss bags exposed in urban areas were significantly higher, while those exposed in rural areas did not differ significantly from the initial content of unexposed moss. Linear regression analysis revealed no significant differences between the average concentrations of elements in *H. cupressiforme* and *S. girgensohnii* moss bags (linearity $R^2=0.94$). It shows similar trends in elements in both moss species. The median values of contamination factors in both moss species ranged mostly from 1.2 to 2.17, indicating the exposure sites show no contamination to slight contamination status (C1 to C2 scales). High values of relative accumulation factors were found for Cr, Cu, Fe, Ni, Sb, and V in moss bags, indicating these elements are the most abundant in most sampling sites, which may increase human exposure through inhalation and could lead to harmful health problems.

Keywords Air pollution · Active moss biomonitoring · *Hypnum cupressiforme* · *Sphagnum girgensohnii* · ICP-MS · TXRF

Introduction

Air quality in urban areas is one of the major concerns of modern society. Particulate matter (PM) is recognized as one important air pollutant that poses major threats to human health (Cohen et al. 2017; WHO 2016). Besides the fraction size, the harmfulness of PM depends on its constituents, including inorganic and organic pollutants. Potentially toxic elements (PTEs) are inorganic substances naturally present

in the environment, but numerous anthropogenic activities concentrated in urban areas have led to their presence in toxic excess (Ali et al. 2019).

In urban areas, PM and its associated PTEs are mainly generated as a result of permanent non-exhaust emissions, such as road surface abrasion, suspension of road dust, wear and tear of vehicular components—tire and brake wear, and exhaust emissions, as well (Pant and Harrison 2013). In addition to these permanent transportation-related emissions in urban settlements, other serious emitters of pollutants are commercial and household heating sources during the winter season, particularly in the Western South East European (WSEE) regions (Belis et al. 2019). Due to numerous pollution sources and complex urban topography, airborne pollutant concentrations are highly variable in space and time, especially in settlements. In addition, the regulatory monitoring networks, based on static gravimetric devices, are reliable but costly and hence scarce and insufficient to be

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representative of the variable spatial and temporal distribution of PM in diversified urban microenvironments (Gozzi et al. 2017). Hence, various approaches to air pollutant monitoring have been developed thus far. Besides ground stations of monitoring networks and satellite observations, the application of biomonitoring is becoming more and more popular (Marć et al. 2015).

Biomonitoring, as a cheap and convenient alternative to traditional sample collection, implies low-cost sampling of systematically distributed organisms or their parts (Markert et al. 2003). Airborne PTEs have been successfully biomonitoring by using mosses, organisms without developed cuticles, roots, or vascular systems, and thus, they rely largely on atmospheric deposition for nourishment. Hence, theoretically, the ambient content of air pollutants should be reflected in the internal composition of moss. Although mosses tolerate high air pollution, they are disappearing from these anthropogenic-pressured areas due to the predominance of paved and landscaped surfaces. To overcome these obstacles, scientists developed so-called active biomonitoring techniques that use moss transplants (moss bag techniques) (Goodman and Roberts 1971; Ares et al. 2012), with the possibility of a precise definition of sampling site and time. The “bag technique” has been widely used and tested in air pollution biomonitoring due to the simplicity of the biomonitor form, easily applicable in any experimental design, which represents a time-integrated response to persistent air pollutants on a scale of several months (Aničić et al. 2007; Aničić Urošević and Milićević 2020). The moss bag technique has been widely tested for monitoring of PTEs in different (micro)environments, industrial (Ares et al. 2011; Salo and Mäkinen 2014; De Agostini et al. 2020), urban (Culicov and Yurukova 2006; Adamo et al. 2003; Vuković et al. 2015; Hu et al. 2018), and agricultural (Milićević et al. 2017; Demková et al. 2017) areas. However, the above-mentioned investigations were case studies without a regional application of the moss bag technique. This study is the first attempt to apply a uniform biomonitor form/species to active biomonitoring of PTEs on a regional scale.

Having in mind that the crucial limiting factor in biomonitoring is the availability of the recommended biomonitor species in the study area, two moss species were used as biomonitors in this study: *Hypnum cupressiforme* Hedw. and *Sphagnum girgensohnii* Russow. The former is widely present in the studied regions, whereas the latter, which is the most recommended species for biomonitoring of air pollutants (Ares et al. 2012; González and Pokrovsky 2014), is endemic in middle, southern, and eastern European countries (except Albania, Greece, North Macedonia, and Turkey) and can be found only at high altitudes (Sabovljević et al. 2008).

Inductively coupled plasma optical (ICP/OES and/or ICP/MS) methods and instrumental neutron activation (INAA)

multielemental analytical techniques are recommended as reference techniques for moss biomonitor elemental determination within the International Cooperative Programme on Effects of Air Pollution on Natural Vegetation and Crops (ICP Vegetation) monitoring implemented regularly on a Euro-Asian scale (Harmens et al. 2013). Apart from these techniques, total reflection X-ray fluorescence (TXRF) and conventional X-ray fluorescence (XRF) could also be used as alternative methods for trace metal determination in different plant tissues. TXRF is an efficient tool to determine the presence of PTEs in different plant tissues (Bilo et al. 2015, 2017). It is successfully used to determine selected elements in atmospheric aerosol precipitations on tree leaves by accurate and precise quantitative analysis of digested samples (Bilo et al. 2017). XRF is a non-destructive technique that, together with TXRF, is a potential tool for the fast and cheap determination of elemental aerosol contamination by using different plant species as biomonitors (Nečemer et al. 2008). Two different moss species and various analytical techniques (ICP-MS, TXRF, and XRF) were applied and compared in this study for the characterization and evaluation of moss element content with the overall goal of assessing the air quality on a regional scale in urban areas of nine South Eastern European (SEE) countries related to the content of PTEs present in atmospheric deposition. The main objectives were to (i) test the application of two distinct moss species in active biomonitoring of PTEs across different urban areas on a regional scale and (ii) evaluate the competitiveness of XRF and TXRF techniques for moss sample analysis in comparison with conventionally used ICP-MS.

Materials and methods

Study area

This study is carried out across the countries, for the most part, situated in South Eastern Europe (SEE) (Fig. 1). Nine urban areas in nine countries were involved in this research: Tirana—TIA (Albania), Tuzla—TZ (Bosnia and Herzegovina), Sofia—SOF (Bulgaria), Zagreb—ZAG (Croatia), Athens—ATH (Greece), Pljevlja—PV and Podgorica—PG (Montenegro), Skopje—SKP (North Macedonia), Belgrade—BG (Serbia), and Ljubljana—LJU (Slovenia). One rural area in Montenegro (Vijenac—VJ) was included in the investigation as a control site (Table S1).

Moss bag preparation

Moss material used for this study was collected at sites remote from anthropogenic pollution sources: *H. cupressiforme* in a national park in Serbia and *S. girgensohnii* in a pristine area in Russia, where the species is widely present.



Fig. 1 The map of study area

The green upper part of the collected mosses was cleaned from extraneous materials, washed thrice with bidistilled water, air-dried, and used for the bag preparations. A portion of such prepared material was kept in laboratory conditions and used as a control sample for measurement of the initial element content in the mosses, necessary for an assessment of net element content after the bag exposure. At the studied site, free-hanging polyethylene net bags of dimensions 7×7 cm were filled with the moss material and exposed at the site (Vuković et al. 2015). Moss bags were exposed at 3 m above the ground level.

The geographic elevations of sampling sites are 20 to 550 m, except Vijenac with an elevation of 1150 m (Tirana 110 m, Belgrade 117 m, Athens 20 m, Skopje 240 m, Ljubljana 295 m, Zagreb 158 m, Sofia 553 m, Podgorica 44 m, Pljevlja 845 m, Vijenac 1150 m, and Tuzla 245 m). The highest elevation is 1150 m which has been accepted as suitable for background site (elevation < 1000 m is permitted for moss biomonitoring according to the ICP Vegetation sampling manual 2010, 2015, 2020) (<https://icpvegetation.ceh.ac.uk/>).

Each moss species was exposed in triplicates in the open spaces of nine SEE cities and one rural area for 2 months during the winter season (from December 1 of 2019 to February 1 of 2020). After the exposure period, the moss samples were dried at 40 °C for 24 h to eliminate wetness and kept under stable laboratory conditions until the chemical analyses. This procedure is usually done in several studies (Sorrentino et al. 2021, Vuković et al. 2016, Esposito et al. 2018, Capozzi et al. 2016, Rivera et al. 2011, Aničić et al. 2009a, b, Temple et al. 1981).

Chemical sample analysis

All moss samples were sent to the laboratory (UNILAB Laboratory (<http://unilab.mk/>) at Goce Delčev University

in Štip, North Macedonia, for ICP-MS analyses of all moss bag samples for chemical determination of potentially toxic elements. Before analysis, the samples were homogenized manually by using plastic gloves. After that, around 0.5 g of each moss sample was placed in Teflon digestion vessels; 7 mL HNO₃ (69%, m/V, Merck, Germany) and 2 mL H₂O₂ (30%, m/V, Alkaloid, N. Macedonia) were added, and the vessels were placed in the rotor of the Mars microwave digestion system (CEM, USA) by applying for the following two steps program: step 1: temperature 180 °C, 20 min ramp time, with the power of 800 W and step 2: temperature 180 °C, 25 min on hold time, with a power of 800 W. Finally, the vessels were cooled and carefully opened. The digests were quantitatively transferred into 25 mL calibrated flasks.

The concentrations of 35 elements (Ag, Al, As, B, Ba, Be, Ca, Cd, Ce, Co, Cr, Cs, Cu, Fe, Ga, Ge, Hg, In, K, Mg, Mn, Mo, Na, Ni, P, Pb, Rb, S, Sb, Sc, Se, Si, Sr, Th, Tl, U, V, Y, and Zn) in dissolved samples were determined by quadruple inductively coupled plasma mass spectrometry (Q-ICP-MS, 7500 cx, Agilent Technologies), which is recommended as a reference technique within the ICP Vegetation monitoring program (Harmens et al. 2013). Other techniques could be used if they provide equal-quality results, particularly in terms of detection and quantification limits and relative standard deviation. A set of selected moss bag samples from the winter sampling session were alternatively analyzed by XRF and TXRF by a Slovenian team to check the potential of XRF and TXRF for PTE determination in the moss bag aerosol study. Both techniques enable multielement simultaneous screening of elements from Al to U. XRF was used for multielement non-destructive screening of fifteen elements like P, S, Cl, K, Ca, Ti, Mn, Fe, Ni, Cu, Zn, Br, Pb, Rb, and Sr, and in the case of TXRF, a similar set of elements screening was performed on decomposed samples of moss bags in nitric acid solution. The XRF sample preparation, experimental instrumental setup, and quantification procedure were described in detail in the publication of Lilek et al. (2022), while the sample decomposition procedure by microwave digestion, TXRF experimental setup, and quantification protocol were described in Likar et al. (2015). Both methods were validated by using SRM materials BCR 482 and NIST 1573a. The standard addition method and reference materials (M2 and M3 moss materials, *Pleurozium schreberi* (Brid.) Mitt., prepared by the Finnish Forest Research Institute (Steinnes et al. 1997), were used for ICP-MS method validation. The recovery of the elements in M2 ranged from 85 to 125%, except for Ce, Ga, Si, Th, U, and Y, while in M3, the recovery range was from 83 to 125%, except for Be, Ce, Co, Ga, Se, Th, U, and Y (Table S2). The concentrations of elements outside of the mentioned recovery ranges are interpreted with caution.

Analytical yield (recovery, R %) was also calculated, using the standard addition method, in a sample of

medicinal/aromatic herbs and spices (*Menta* spp. inter-laboratory sample). The statistical calculations are presented with the average of the calculated analytical yields at all two levels of concentrations of (a) trace and (b) macro elements. The summary data from the conducted analysis is given in Table S3. The satisfactory criterion is analytical yield in the range of R: 85–115% or allowable yield error not higher than $\pm 15\%$. A series of control samples were analyzed by the ICP-MS method to determine the lowest detectable background of the applied instrumental technique. To determine the limit of detection (LOD), a blank sample was used (blank, 2 mL H_2O_2 , and 5 mL HNO_3 , totally diluted to a final volume of 25 mL), 10 replicates with 3 runs for each measurement. The $3 \times \text{SD}$ method was used to determine LOD (Table S4).

Data processing

For data processing, Statistica 8.0 (Stat Soft Inc., Tulsa, OK, USA) and MINITAB 19 software were used. The control of the moss bag experiment was not only the initial element content (C_{initial}) in the unexposed moss material but the limit of quantification of the moss bag technique (LOQt) was calculated following the equation:

$$\text{LOQt} = xCi + 1.96sCi \quad (1)$$

where xCi is the mean value of the initial concentration in the unexposed moss (control samples) for each element determined, while sCi is the corresponding standard deviation. Calculation of the LOQt enables a clear distinction of the element concentrations in the exposed and unexposed moss material; thus, the “noise” associated with the methodology of moss bag technique is already included in data interpretation. The strict definition of LOQ comes from analytical chemistry, which defines LOQ as $10sCi$, which can be detracted in the active moss biomonitoring to $1.96sCi$ due to a normal element distribution in the unexposed moss material (Ares et al. 2015).

A descriptive statistic is applied to the concentrations of the elements, through the mean, median, and standard deviation, while the variation of concentrations was presented by the coefficients of the variance, skewness and kurtosis. Spatial analysis is applied to investigate the spatial differences in element content among studied urban areas.

As the data are not normally distributed, tested by MINITAB 19 probability plot, Mann–Whitney U test was used to check for significant differences ($p < 0.05$) in the mean elemental concentrations between two moss species (*H. cupressiforme* and *S. girgensohnii*) exposed at the same sites during the same time. To assess the specific associations of the elements, Pearson’s correlation analysis

between the element concentrations was conducted. All tests were performed at a confidence level of $p < 0.05$.

As a measure of moss capability for element accumulation, relative accumulation factors (RAF) were calculated according to the equation:

$$\text{RAF} = (C_{\text{exposed}} - C_{\text{initial}}) / C_{\text{initial}} \quad (2)$$

where the element concentration in the moss after exposure (C_{exposed}) was reduced and divided by its concentration in the moss before exposure (C_{initial}). According to the RAF values, the classification of elemental enrichment in moss indicates a slight elemental enrichment for $0.5 < \text{RAF} < 1$ and a considerable elemental enrichment for $\text{RAF} > 1$ (Vuković et al. 2015).

The pollution level and the effect of anthropogenic sources are assessed by the contamination factors (CF) calculated as the ratio of the site element concentration (C_i) in the exposed moss to the respective background content of the element in unexposed moss material (Hakanson 1980).

$$\text{CF} = C_{i,\text{el}} / C_{\text{background,el}} \quad (3)$$

The scale for CF categories proposed by Hakanson (1980) was also applied in the atmospheric deposition study (Qarri et al. 2019, Allajbeu et al. 2017, Fernández and Carballeira 2001), which comprises five categories: C1: $\text{CF} \leq 1.2$, no contamination; C2: $1.2 < \text{CF} \leq 2.2$, slight contamination; C3: $2.2 < \text{CF} \leq 3.3$, moderate contamination; C4: $3.3 < \text{CF} \leq 4.3$, severe contamination; and C5: $\text{CF} > 4.3$, extreme contamination (Hakanson 1980).

Pearson’s correlation is used to evaluate the relationship between the elements and to differentiate between the levels of correlation, nominated as very strong, strong, and moderate correlations. A multivariate statistical method, factor analysis (FA), was used to investigate the effects of the sources of contaminants on air pollutants. FA is applied to the dataset of element concentrations recorded in both moss species, which were exposed at 45 sites in SEE countries to assess the likely sources of metals. The data matrix obeys Thurston and Spengler (1985) requirement, with the number of rows (sampling sites) at least three times higher than the number of variables.

Results and discussion

Element content in exposed moss bags—initial element content, LOQt

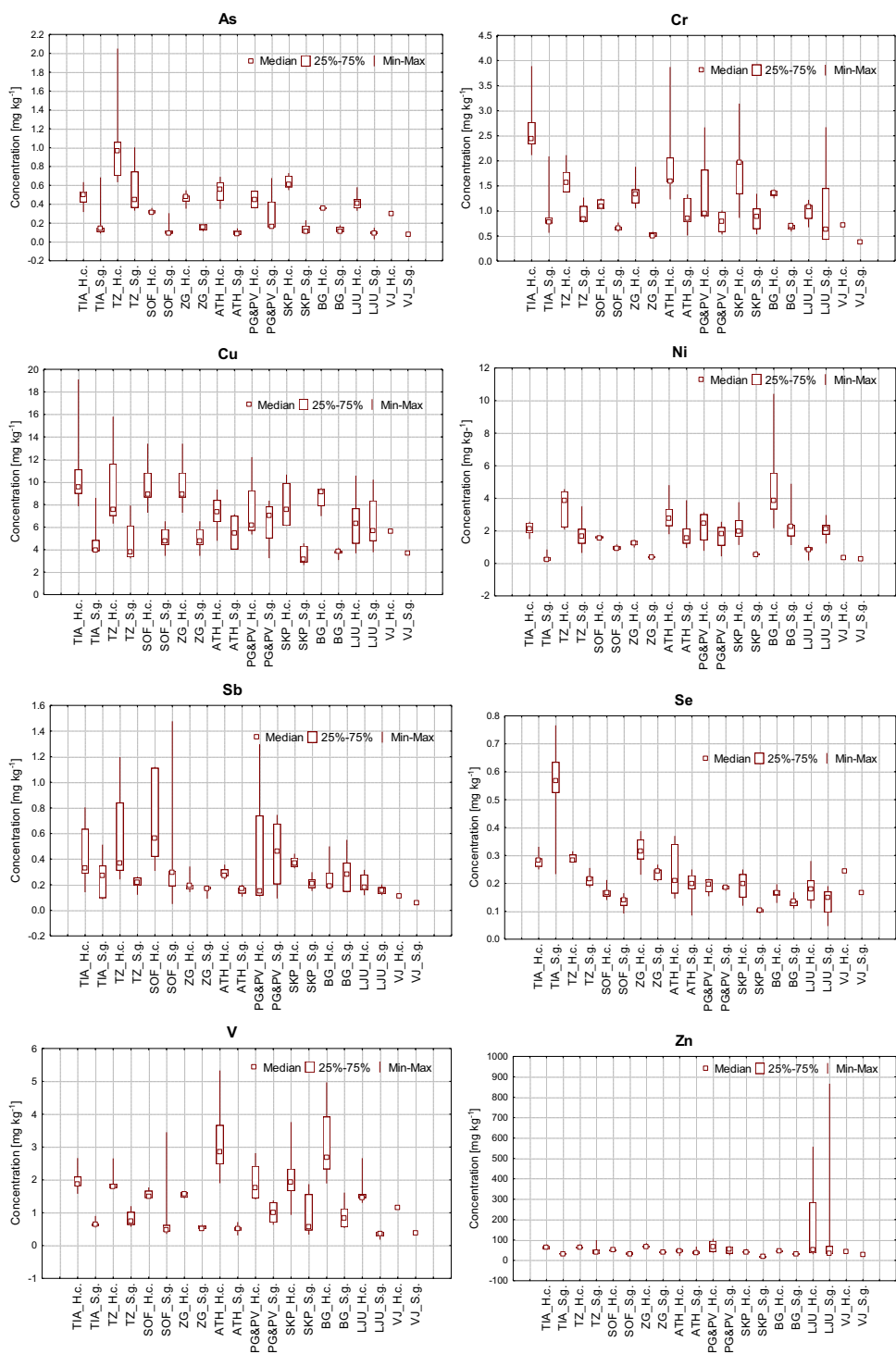
The concentrations of 35 elements measured in two moss species (biomonitors) exposed across different urban areas of SEE during the winter season are presented in Table S5 and Fig. 2. The results showed that the majority of the

elements significantly enriched the exposed moss bags in comparison with the initial element concentrations, at least at one sampling site in each of the studied urban areas. The only element that was not accumulated in the mosses during exposure time was Sc. The element concentrations found in the mosses exposed at the rural site (Vijenac)

were at the level of the initial element content which confirmed the background status of the rural site.

The average concentrations of the elements in moss bags after 2 months (December 2019 and January 2020) of exposure in nine cities of SEE (Table S6 and Table S7) were used to compare the levels of atmospheric pollution evaluated by two moss species, *H. cupressiforme* and *S. girgensohnii*. The

Fig. 2 Box and whiskers plots of the elements (As, Cr, Cu, Ni, Sb, Se, V and Zn, in mg/kg) determined in the mosses (*H. cupressiforme* and *S. girgensohnii*) exposed at the sites within each of studied urban area (TIA, TZ, SOF, ZG, ATH, PG&PV, SKP, BG, LJU) and the rural one (VJ) during winter 2019/2020



concentrations of B, Ba, Bi, Ce, Co, Cr, Cu, Er, Fe, Mg, Na, Ni, Sb, Si, V, and Zn in the exposed moss bag were mostly (in more than 94% of sampling sites) higher than the respective initial element concentrations. For Ag, Ba, Be, Bi, Ga, Sb, U, and Zn in both moss species, as well as for B in *S. girgensohnii* high variation among exposed sites (CV % > 75%) was found, indicating the data are affected by several factors, while the data of elements with low concentration in moss bag samples, like Ag, Ba, Be, Bi, Ga, and U, are affected by high uncertainty of the analysis. The average concentrations of the elements in two studied moss species are compared by correlation analysis and the Man-Whitney test. No significant differences were found between the average concentrations of elements in *H. cupressiforme* and *S. girgensohnii* moss bags ($p=0.488 > 0.05$). It is confirmed by linear regression analysis, which resulted in very high linearity ($R^2=0.94$), indicating the same trends of variations of the element concentrations in both moss species (Fig. 3). In general, the concentration data of this environmental study follow lognormal distribution or nearly so, and the logarithmic concentrations data are approximately normal, or Gaussian, over the observed range (Ott 1990). The variability of the observed data is generally reduced by taking average values of increasing numbers of measurements. It may be of considerable benefit to smooth the data before performing linear correlation analysis (Dunlap et al. 1983).

H. cupressiforme vs. S. girgensohnii biomonitor features

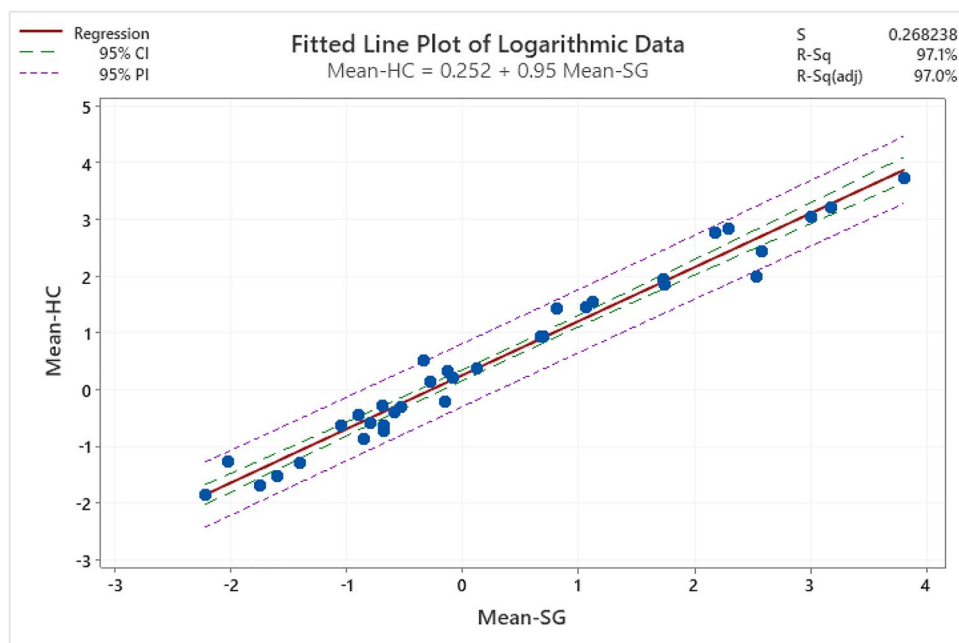
A lack of the most recommended biomonitor moss genera in the studied region (*Sphagnum*) implied the necessity for testing alternative moss species (*H. cupressiforme*) for

monitoring purposes. The results of this study show slightly different patterns of element enrichment by two studied moss species (Table S6 and S7). This discrepancy in the element composition between the mosses exposed at the same sites can be a consequence of different initial element content in the unexposed moss materials used for the bag preparation, moss morphological features, and growth rates (Zechmeister 1995), as well as environmental pollution of the pristine and background areas. Namely, the initial moss element content defines the moss absorption capacity to the elements. The lower initial element content suggests that cation-exchange sites were not saturated with basic cations, which possibly influenced the better element adsorption capacity. More efficient entrapment of elements by moss with low initial element content has also been shown in previous research (Culicov and Yurukova 2006; González and Pokrovsky 2014).

RAF and CF

The calculation of RAF excludes the influence of the initial element concentration from the final element content in the mosses and testifies to the ambient element level to which the moss bags were exposed. Except for initial element concentration, another, stricter criterion for estimation of element enrichment in moss is its LOQt value (Eq. 1). The RAFs of the selected PTEs (As, Cr, Cu, Ni, Sb, Se, V, and Zn) with proven human toxicity (IARC 2011) are presented as box and whisker plots, describing the range of the concentrations for each of the studied urban areas and the rural one (Fig. 4). The distribution of the moss element concentrations within the studied areas

Fig. 3 Linear regression of average concentrations (logarithmic data) of elements in both moss species, *H. cupressiforme* (*H.c.*) and *S. girgensohnii* (*S.g.*)



is element-specific, either uniform for the studied areas (e.g. Zn, except for LJU/SLO moss bag samples) or scattered (e.g. Cu). These findings suggest that the sources of certain elements are probably uniform or not across particular areas.

The spatial distributions of RAFs at studied sites are presented by RAF plots (Figs. 5 and 6).

High RAF values were found for Co, Cr, Cu, Ni, Sb, and V in both moss species indicating these elements as the most abundant at most of the sampling sites. The sequence of median values of RAFs in *H. cupressiforme* moss bags is $V > Ni > Sb > Cr > Cd > Co > As > Cu > Fe > Zn > Ti > Se$, and $Sb > Ni > Zn > Fe > Cr > Co > Cu > V > As > Ti > Cd$ in *S. girgensohnii* moss bags. Differences between RAFs of elements in both moss species are tested by linear

Fig. 4 Box and whiskers plots of RAF values for the selected elements (As, Ba, Be, Cd, Cr, Cu, Ni, Sb, Se, V, and Zn) determined in the mosses (*H. cupressiforme* and *S. girgensohnii*) exposed at the sites within each of studied urban area (TIA, TZ, SOF, ZG, ATH, PG&PV, SKP, BG, LJU) and the rural one (VJ) during winter 2019/2020

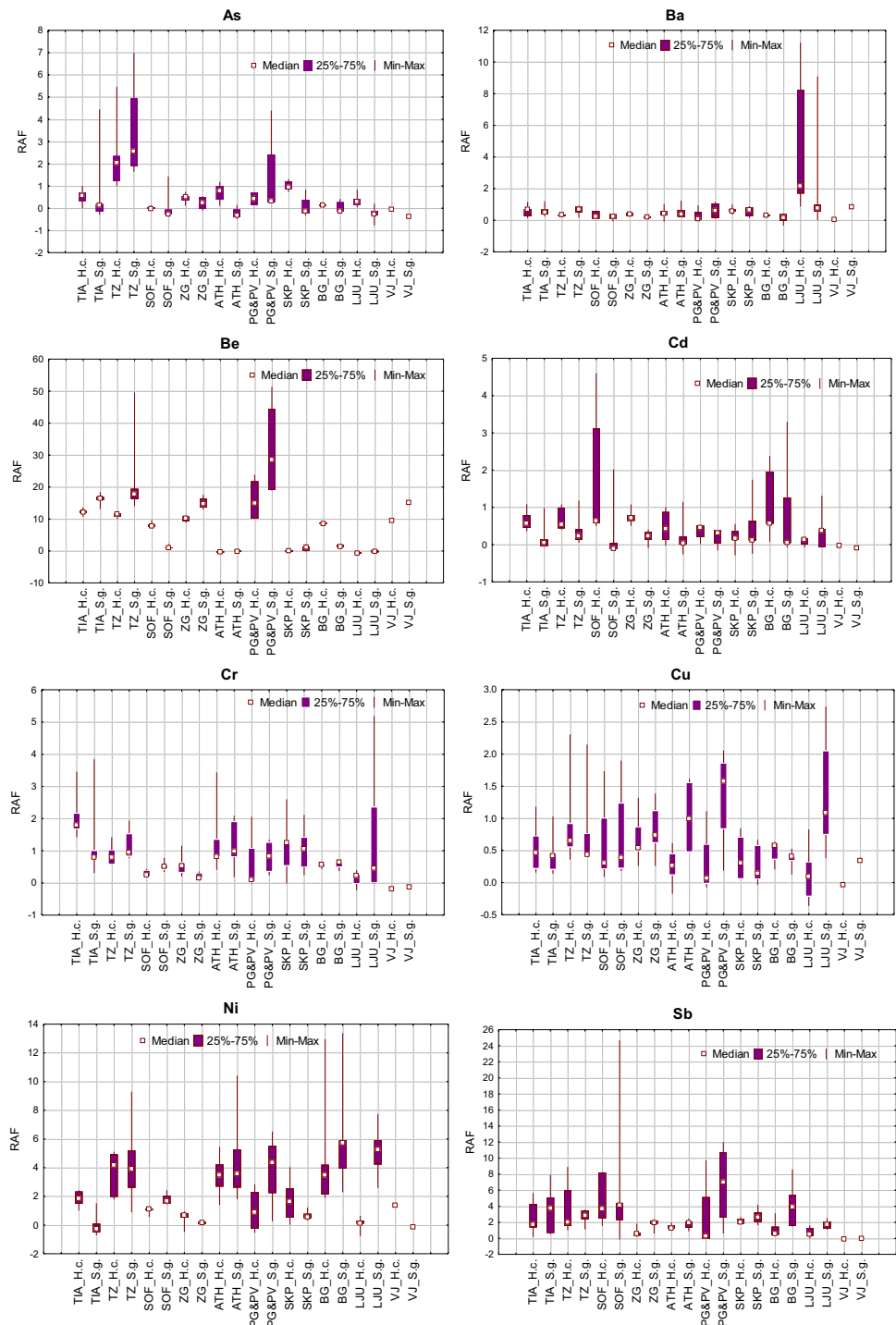
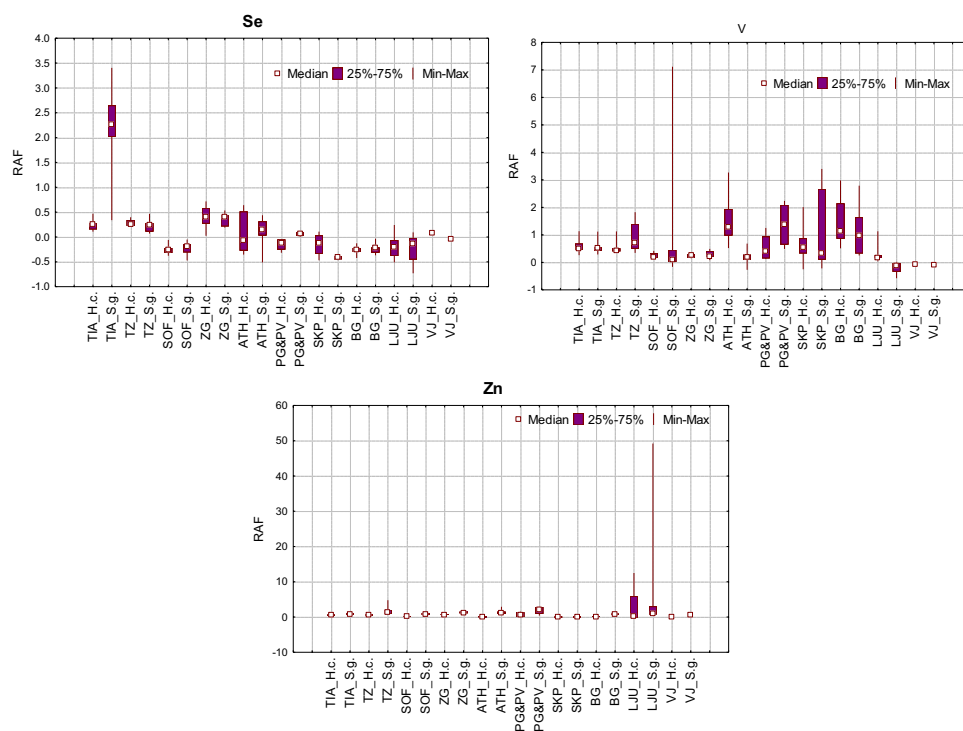


Fig. 4 (continued)



correlations of the data of *H. cupressiforme* and *S. girgensohnii* mosses (Table S8). The most enriched elements in the mosses for studied urban areas are described in the following paragraphs for each country in particular. There are complex factors affecting the concentrations of the elements in the exposed moss samples. Airborne content of the elements is the main factor affecting the content of elements in atmospheric deposition. Besides the meteorological factors such as weather conditions responsible for wet and dry deposition, wind speed and direction, temperature affect the content of elements in the exposed moss. We are aware of the complexity of meteorological and topographic factors influencing the moss element content. However, in the experiment, we fixed, at least, the same moss species used, the same height of moss bag exposition, the exposure time, and local conditions in sense of the moss bag exposition in an open space, not under a roof or any tree crown. We did not discuss the dependence of PTEs content in the moss from meteorology having in mind that most bags were exposed in the same climate zone at least, and mainly in continental conditions.

Contamination factor spatial plots were drawn to investigate the distribution of CFs at all exposure sites. As the CFs of elements in both moss species showed very high similarity between them (tested by linear regression, Table S9), the *H. cupressiforme* data are used for CF plot representation (Fig. 7).

The sequence of median values of CFs on *H. cupressiforme* moss bags resulted in Ni > Sb > Ti > Cu > Cr > Cd

> Se > Fe > V > Zn > As, and Ni > Ti > Cd > Se > Cr > Cu, Zn > Sb > Co > As > V on *S. girgensohnii* moss bags. The median values of elements in both moss species ranged from 1.2 to 2.17 (Table S10), indicating slight pollution status (C2 scale). In general, the exposure sites exhibit no contamination to slight contamination status (C1 to C2 scales). However, there were certain “outlier” sites with extremely high pollution levels (Table S10 and S11).

Most of the winter exposed moss bag samples showed no/or slight contamination scale for As, Cd, Co, Cu, Fe, Se, Zn, and V elements, except for distinct stations. Only one site, the TZ-4 urban area, belongs to the extreme contamination scale for As. It probably originated from the dense households in the area that burn coal and wood for heating during the winter months. The same, extreme contamination of Cd was found at the SOF-2 site. This site is positioned in an area with intense traffic flow and related vehicular emissions on the cloverleaf interchange leading to the A1 highway, located less than 1 km away from this site. Besides the traffic emissions, another probable source of Cd at this site is probably affected by fossil fuel combustion for domestic heating. Moderate Cd contamination was recorded at sites BG-4 and BG-5, which are both suburban municipalities of Belgrade. BG-4 is rather situated in a village than a town settlement, mainly a residential area with low traffic intensity but with possible local pollution sources (possible local waste incineration). In the winter season, active individual house heating sources are burning a variety of fuels (wood, coal, pellets, and crude oil). In addition, this site is in the

Fig. 5 RAF spatial distributions of Cd, Cr, Cu, Ni, Sb, Se, Ti, V, and Zn (*H. cupressiforme* moss bags). Exposure sites: 1 to 5—TIA-1 to TIA-5; 6 to 10—TZ-1 to TZ-5; 11 to 15—SOF-1 to SOF-5; 16 to 20—ZAG-1 to ZAG-5; 21 to 25—ATH-1 to ATH-5; 26 to 30—PG-1 to PG-5; 31 to 35—SKP-1 to SKP-5; 36 to 40—BG-1 to BG-5; 41 to 45—LJU-1 to LJU-5

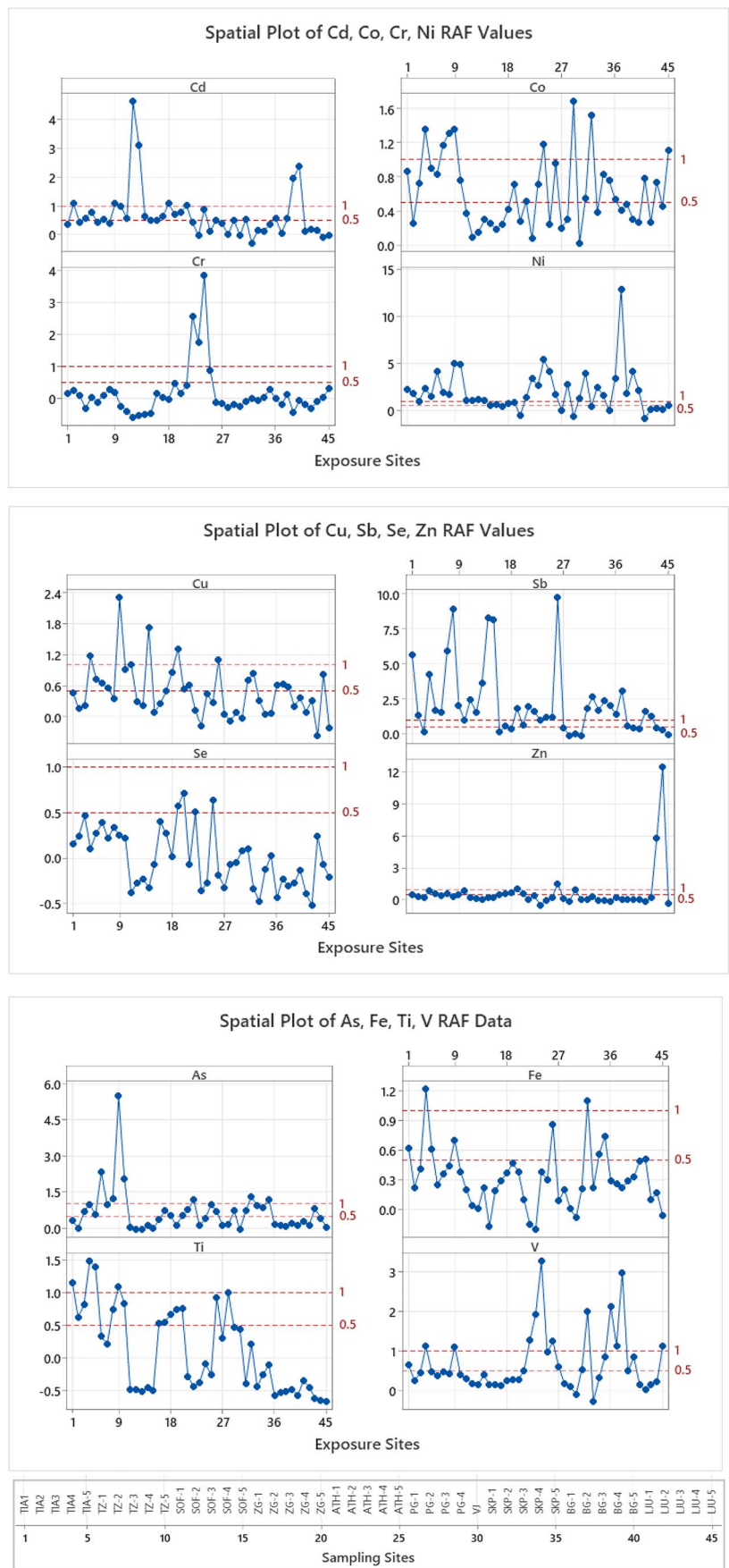


Fig. 6 RAF spatial distributions of Cd, Cr, Cu, Ni, Sb, Se, V and Zn (*S. girgensohnii* moss bags). Exposure sites: 1 to 5—TIA-1 to TIA-5; 6 to 10—TZ-1 to TZ-5; 11 to 15—SOF-1 to SOF-5; 16 to 20—ZAG-1 to ZAG-5; 21 to 25—ATH-1 to ATH-5; 26 to 30—PG-1 to PG-5; 31 to 35—SKP-1 to SKP-5; 36 to 40—BG-1 to BG-5; 41 to 45—LJU-1 to LJU-5. (The codes and names of the exposed sites are shown in Fig. 5)

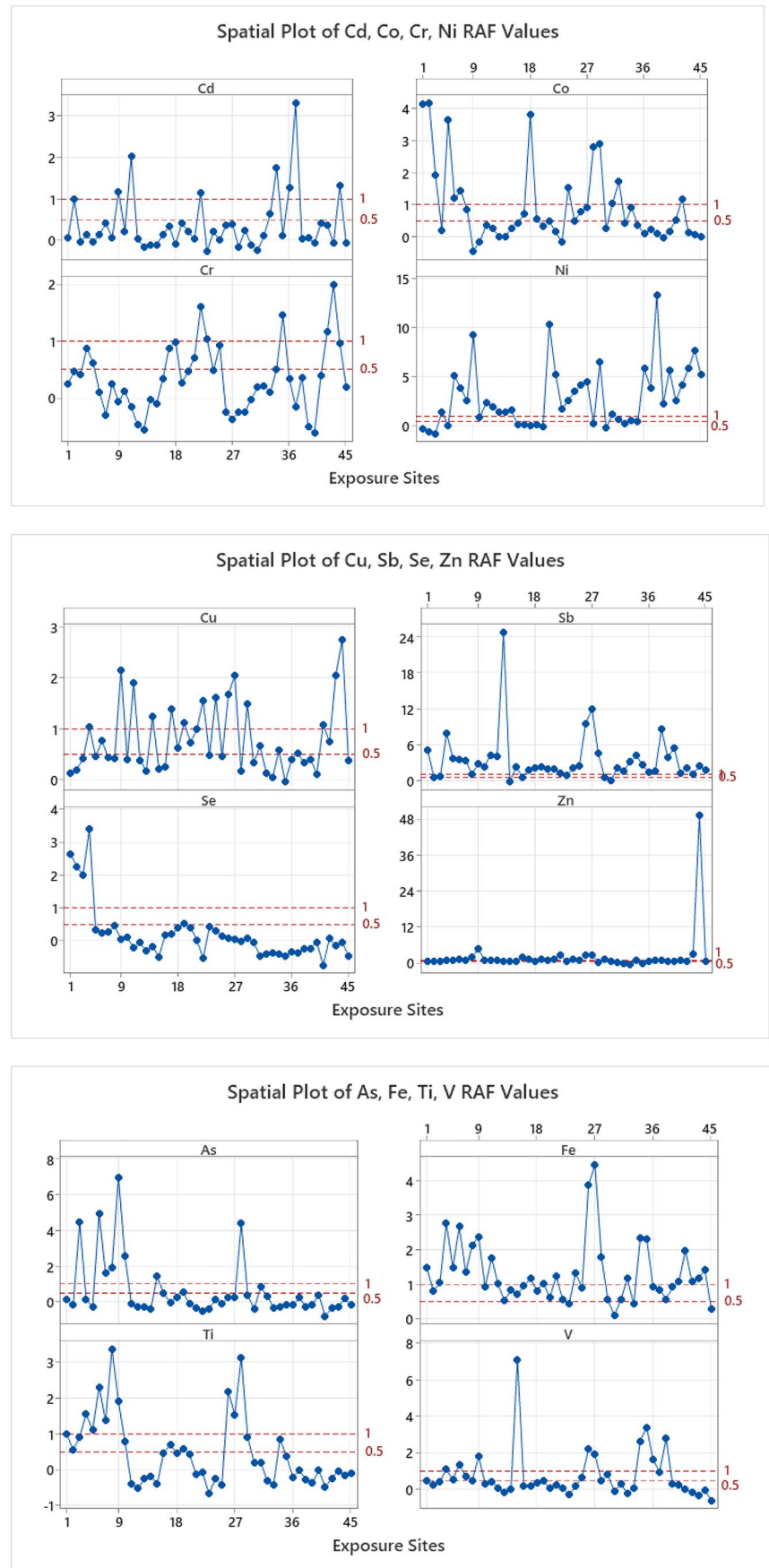
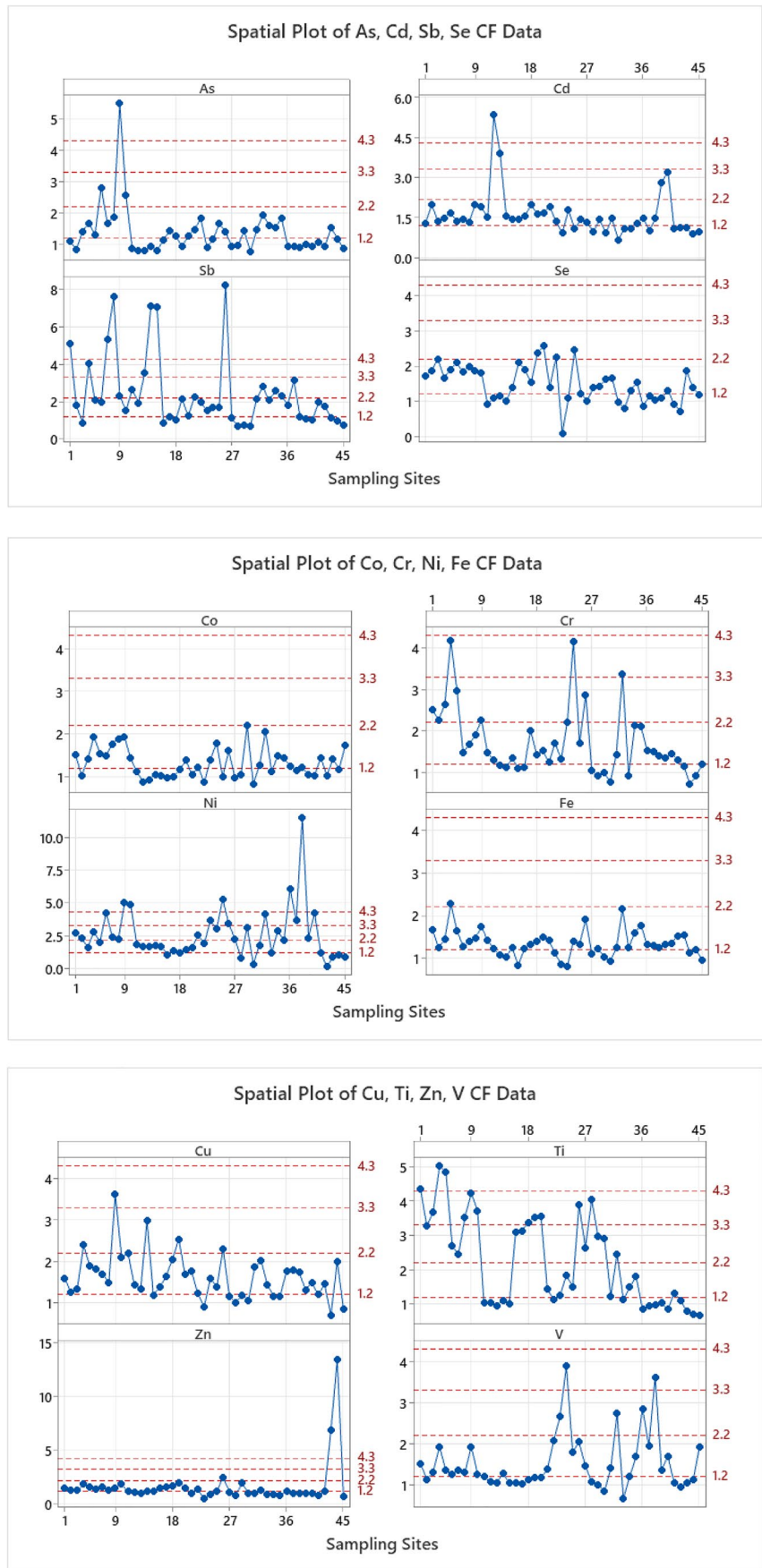


Fig. 7 CF spatial distribution plot of As, Cr, Cu, Ni, Sb, Se, V, and Zn along *H. cupressiforme* moss bags exposure sites (the codes and names of the exposed sites are shown in Fig. 5)



line of wind flow coming from the direction of the main Belgrade city landfill (“Vinča”), where the burning of diversified urban waste is common.

High Zn content was found in moss bags from two locations in Ljubljana (LJU-3, Hrastje, and LJU-4, J. Stefan Institute). LJU-3 site is located close to numerous gardens where people grow vegetables for their consumption. In almost every garden, there is a small garden house built up from old wooden parts of old painted furniture. Occasionally, the gardeners repair their houses and burn the rest of the wooden material. It is suspected that Zn originated from the ZnO compound used as a paint additive. The identical combustion source of old furniture parts explains the high Zn content found in the moss bags from the Institute location (LJU-4). In the vicinity of this site, there is a spot where people are illegally burning old painted furniture parts in a non-standard practice.

Severe contamination was found for Cd at BG-5 and SOF-3 sites. BG-5 is positioned close to the thermal power plant (TPP) “Kolubara A” and the largest mining basin of lignite coal in Serbia. Besides non-ferrous metal production that is the major source of cadmium emissions to the air, combustion of coal (BG-5) and oil, together with waste incineration (BG-4) are assumed to be responsible for the presence of this element in a technosphere or an urban environment (Pacyna and Pacyna 2001). SOF-3 site is a residential zone in the vicinity of the Sofia industrial area and the TPP Sofia-East Thermal Power Plant.

The situation in different urban areas regarding Cr, Cu, Ni, Sb, Ti, and V shows a few stations with no/or slight contamination scales. Only two stations (BG-1 and BG-3) show Ni extreme pollution. Sites TZ-3, SKO-1, SOF-4, SOF-5, and PG-1 belong Sb extreme pollution scale. Relatively high concentrations of Ni at all studied sites in Belgrade, except BG-4, can be related to fossil fuel consumption as a heating source (Pacyna and Pacyna 2001), in both centralized heating systems and individual household heating units. Extreme contamination by this element was observed at the BG-1 site, which represents an urban residential area with intense traffic flow and predominantly individual households' heating sources during the winter months, with an expectedly high level of air pollution in winter.

Most of the sites showed moderate to severe Cr and Ni contamination, which could be attributed to vehicular emissions (Taghvaei et al. 2019) and road traffic (Manousakas et al. 2021). Pateraki et al. (2019) have also detected traces of Cr and Ni at different monitoring heights in the same roadside environment. Ni is an indicator of road dust and vehicular exhaust. The sites ATH-4 and ATH-5 are known for high vehicular traffic. The moderate contamination of Cr can be attributed to anthropogenic emissions, especially road traffic (Manousakas et al. 2021; Diapouli et al. 2016). All the stations with high Cr and/or Ni content are positioned close

to heavy-traffic roads. The site ATH-3 (Edessis 6, Galatsi) is close to roads with high vehicular traffic. The moderate contamination of Cr and the severe contamination of Ni can be attributed to vehicular emissions (Taghvaei et al. 2019). Pateraki et al. (2019) have also detected traces of Cr and Ni at different monitoring heights in the same roadside environment. Besides, the relatively high contents of Cr and Ni in the moss bags of Skopje are mostly linked to the lithogenic origin of wind-blowing fine soil dust particles. Skopje region geologically belongs to the Vardar Zone as a tectonic unit rich in Cr and Ni (Stafilov and Šajn 2016, 2019; Stafilov et al. 2017, 2019).

Pearson correlation analysis of the elements was conducted on the elements of moss bags exposed in Tirana (Table S12 and Table S13) to investigate the associations of the elements and to explain the sources of higher Cr, Sb, and Ti content in the selected moss bags. High Cr content was found in all the moss bags exposed in Tirana. Strong and very strong correlations ($r > 0.79$, $p = 0.000$) were found between Cr and Co, Fe, Ti, V, Zn, and As. The association of Cr with the lithogenic and crustal elements (Ti and Fe) could be linked to the roadside enrichment of soil dust fine particles and natural emission sources.

Extreme contamination of Sb in moss bags exposed at TZ-3, SKO-1, SOF-4, 5, PG-1, TIA-1, and TIA-4 sites is probably linked with heavy traffic roundabouts. In recent decades, Sb has been considered a key tracer of traffic air pollution (Grigoratos and Martini 2015). Sb in the form of stibnite (Sb_2S_3) is employed as a lubricant to reduce vibrations and improve friction stability (von Uexkull et al. 2005; Bukowiecki et al. 2009). The obtained results for Sb at SOF-5 are located on the outskirts of the city, in Vitosha Mountain, and the lithology of the region cannot explain the obtained results for Sb (Vladimirova et al. 2010). It is probably linked to the transport of Sb from other areas as well as the effects of wind speed and direction during the study period. High Sb content was found at TIA-1 and TIA-4 sites, which could be related to the automotive brake abrasion dust, tire wear, mostly of old vehicles with coated tires, and brake linings as important sources of Sb in Tirana. Besides, Sb showed a very strong correlation with Ni ($r = 0.903$, $p = 0.000$). The Sb-Ni association in urban areas could be derived from traffic emissions as part of fuel oil burning. In addition, specific elements (Sr, Ba, Sb, Pb, Na, K, and Cu) are added to fireworks, producing differently colored fireworks, so it is therefore unsurprising to find higher concentrations of these elements following fireworks displays (Cao et al. 2017). The moss bags were exposed during December–January when Tirana citizens traditionally put fireworks on the occasion of New Year.

Severe contamination of Cr, Cu, Ni, and Zn was found at SKO-1 and PG-1 sites. It could be linked with the finest fractions of urban and motorway dust contaminated with Cr

and Cu, which are known as tracers of brake wear (Adamiec et al. 2016); Zn is the most abundant heavy metal from tire wear; asphalt and sandpaper-like effects are significant sources of Ni in road dust (Ozaki et al. 2004), while road bitumen contains prominent concentrations of Ni and Zn (Gadd and Kennedy 2000; Duong and Lee 2011).

Sources identification of metals by factor analysis

Three main factors were extracted from the FA and CF data matrix. The profile of each factor and the contribution of the elements are shown in Table 1.

The first factor (F1) represents 28.4% of the total variance. It is characterized by the presence of crustal elements Fe, Ti, Cr, and Co with a contribution sequence of Fe > Ti > Cr > Co. The presence of Cr and Co can be both from natural and anthropogenic sources. The association of these elements could assign to crustal origin in the form of fine soil dust particles in the air. Despite this, some industrial emission contamination could be present in the studied areas. This association could also be assigned as a geogenic factor. The lower contribution comes from Sb and Cu. The association of Sb and Cu in this factor could be assigned to break lining origin which could be considered as the main source for Cu and Sb in a heavy traffic environment (Hjortenkrans 2008).

The second factor (F2) represents 18.8% of the total variance. It is characterized by the presence of V, Ni, and Se with a contribution sequence of V > Ni > Se. Because of the high loadings of Ni and V in this factor, they could be assigned to fossil fuel combustion and traffic emission sources. A lower contribution to this factor comes from Se.

Table 1 Sorted Varimax rotated factor loadings and communalities extracted from FA of the correlation matrix of most toxic elements (Cd, Co, Cr, Cu, Fe, Ni, Sb, Se, Ti, Zn, V)

Variable	F1	F2	F3	Communality
Fe	0.839	0.000	0.000	0.716
Cr	0.779	0.000	0.000	0.732
Ti	0.765	0.000	0.000	0.737
Co	0.663	0.000	0.000	0.623
Cu	0.622	0.000	0.000	0.465
Sb	0.438	0.000	0.000	0.322
V	0.000	0.898	0.000	0.855
Ni	0.000	0.751	0.000	0.596
Se	0.000	0.533	0.000	0.454
Cd	0.000	0.000	0.787	0.646
Zn	0.000	0.000	0.508	0.311
Variance	3.119	2.064	1.274	6.457
% Var	0.284	0.188	0.116	0.587

It could be derived from coal and petroleum burning, as well as waste burning.

The third factor (F3) represents 11.6% of the total variance. It is the weakest factor that is characterized by the presence of Cd and Zn anthropogenic elements. The sequence of these elements in this factor is Cd > Zn. Cd and Zn are typical anthropogenic elements from traffic emission sources. The association of these elements could be assigned to tires as the main source of Zn and Cd.

Investigation of performance characteristics of alternative analytical methods TXRF and XRF for moss sample analysis

Tables S14 and S15 show concentrations of S, K, Ca, Mn, Fe, Zn, Rb, and Sr determined by XRF and TXRF in moss samples from two studied sites in Ljubljana (Slovenia)—Hrastje (*S. girgensohnii*) and IJS (*H. cupressiforme*), which characterized high Zn concentrations measured by ICP-MS. Besides, the results of BCR 482 lichen standard and NIST 1573a (tomato leaves) reference material analysis are presented in Tables S16 and S17, to demonstrate and critically evaluate the competitiveness of XRF and TXRF for moss sample analysis. Uncertainty, accuracy, optimal concentration range, LODs, as well as advantages and disadvantages of each method are compared and discussed. A comparison of XRF and TXRF results (Tables S15 and S16) reveals good agreement of all measured elements among both applied techniques. Increased Zn content (discovered by ICP-MS measurements) was detected and quantified by both techniques indicating the preparation of samples and their homogenization was satisfactory, and the decomposition procedure was efficient and well performed in the case of TXRF. Destructive and non-destructive ways of analysis and obtained results were within allowed uncertainty limits. Both techniques offer a screening of elements from Z=16 (S) to Z=92 (U) in the concentration range of a few percent to a few mg kg⁻¹ simultaneously. Tables S15 and S16 indicate the competitiveness of both techniques for the analysis of certified plant material samples with the organic matrix similar to the moss samples type used in this study. In Table S16, the Lichen BCR standard reported only certified value for Zn, other presented element values were informative. In the case of the NIST 1573a, all values were certified, except for S and Sr. Values obtained by both techniques are in good agreement with the BCR certificate, indicating satisfactory accuracy of both techniques. We noticed that Cl and Br contents analyzed by TXRF in decomposed samples were significantly lower than those obtained nondestructively by XRF indicating that during the digestion procedure the mentioned elements were diminished. The preparation of solid samples by wet digestion requires the application of time-consuming chemical procedures that require various highly

pure and costly mineral acids, equipment, and qualified personnel for sample preparation and handling. In standard XRF only simple sample preparation including grinding, homogenization, and palletization was applied. Regarding the sensitivity of XRF against TXRF, its sensitivity was one order of magnitude higher than XRF. TXRF requires a minute sample amount in liquid form for analysis; usually few μL of decomposed sample deposited and a dried quartz substrate is sufficient for TXRF determination. However, the mentioned superior TXRF sensitivity diminished due to the dissolution of the sample during the sample decomposition procedure concluding XRF and TXRF sensitivity were equal for the analysis of moss samples. LODs for the measured elements were among 1–10 mg/kg. TXRF analysis was faster 300–500 s, while XRF determination requires a minimum of 6000 s for two measurements in Fe-55 and Cd-109 excitation mode for multielement determination of light Z and heavier Z elements. The estimated uncertainty budget of the XRF and TXRF analysis was assessed to be around 10% and it was higher than those reported by the ICP-based method (around 5%). Although XRF-based techniques (especially standard XRF) were not such sensitive as AAS, ICP-AES, or ICP-MS, they are much cheaper and environmentally friendlier, and due to the simplicity of the sample preparation procedures, they enable analyses of large numbers of samples, which is a common requirement in environmental monitoring.

Conclusion

In this study, airborne PTE pollution during the winter season (December 2020–January 2021) was estimated by moss bag samples exposed in ten SEE cities around dense traffic, urban and industrial areas, and at a background site in Montenegro (rural area). Two distinct moss species (*H. cupressiforme* and *S. girgensohnii*) were employed to prepare moss bags used for the active biomonitoring of PTEs. The concentrations of PTE in moss bags exposed at the rural site were at the level of the unexposed moss, while prominent accumulations of PTEs were recorded in the moss bags exposed at the urban sites.

No significant differences were found between average concentrations of elements in *H. cupressiforme* and *S. girgensohnii* moss bags ($p = 0.488 > 0.05$), confirmed by linear regression analysis, which resulted in very high linearity ($R^2 = 0.94$), indicating the same trends of element variations in both moss species. The elements like Ag, Ba, Be, Bi, Ga, Sb, U, and Zn in both mosses showed high variation among studied sites ($\text{CV} \% > 75\%$), suggesting that moss samples were affected by several factors, while spatial fluctuation of elements with low concentrations (Ag, Bi, Cs, Ga, and U) in mosses was probably affected

by high uncertainty of the analysis, so these elements are not included in this study.

The differences between the accumulation capacities of elements in both moss species were tested by RAF values and linear correlation analysis of the average content dataset. High RAFs were found for Cr, Cu, Fe, Ni, Sb, and V, indicating these elements as the most abundant at most sampling sites. Similar accumulation capacities were found, particularly for Zn, Ti, As, Ni, and Fe in both moss species. The same contamination levels of the elements (CFs) were found by both moss species, except for As and Sb. The median CFs in both moss species ranged mostly from 1.2 to 2.17, indicating no contamination to slight contamination status (C1 to C2 scales) of the studied sites.

RAF and CF values revealed some elements with increased levels in SKP, TZ, SOF, and BG in comparison to ZAG, LJU, ATH, and TIR. It could probably be linked to different fuels used as heating sources during the wintertime. We believe that the main sources of air pollution during the wintertime are heating sources besides traffic. The wintertime of PM_{2.5} in 2019/2020 was characterized by prominent air pollution for western Balkan countries, with a PM_{2.5} sequence of PM_{2.5} as SKO > TZ > SOF > BG > LJU > ATH > TIA (<https://www.numbeo.com/.....>), and it is a good result that the moss bag biomonitoring confirms that.

The urban soil and roadside dust are usually heavily affected by historical total element concentrations, so the soil dust emission could be considered a strong factor affecting the level of the PTE content in the moss bag samples. It is clearly stated by the high correlations between the crustal elements such as Fe, Ti, Cr, and Co. Besides, tire wear is the main source of Zn and Cd, while brake linings are the main source of Cu and Sb in a heavy traffic environment.

The study performed to assess the suitability of XRF and TXRF methods for moss bag analysis reveals that both methods applied to the mentioned task. They are a fast and cheap alternative, especially XRF for fast screening of a large number of samples, as is the case in such aerosol studies. Both methods enable the analysis with sufficient sensitivity to identify and assess the possible PTE aerosol pollution in a concentration range higher than a few tens of ppm.

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Declarations

Ethics approval and consent to participate All procedures performed in this study were following the ethical standards of the institutional and/or national research committee. All authors agree to participate in this research. They have read and agreed to the published version of the manuscript.

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