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## Atmospheric deposition of potentially toxic elements over the territory of Serbia assessed by moss biomonitoring in five-year time: 2015 vs. 2020

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**Abstract:** The presented research, performed under the framework of the ICP Vegetation program in Serbia, had a goal to provide field-based evidence of spatial patterns and temporal trends of some potentially toxic element deposition, using naturally growing moss (*Hypnum cupressiforme*), as a biomonitor in surveys conducted in 2015 and 2020. The results showed a decline of the element concentrations in the moss with time for Cr (42 %), Cu (39 %), Fe (22 %), Pb (10 %) and Zn (54 %), a decrease for Cd (18 %), while staying at the same level for As and V. The concentrations of examined elements in the moss samples were comparable to those found in the neighbouring countries, with the median country values often being five or more times larger than in the pollution background countries like Switzerland and Norway. Calculation of ecological implication indices generally suggested the presence of low to moderate pollution all over the study area, with severe contamination with As, Cr, Cu and Pb at some studied locations in the eastern and northern parts of the country.

**Keywords:** air pollution; PTEs; moss survey; ICP vegetation; *H. cupressiforme*.

### INTRODUCTION

Air pollution is perceived as the second biggest environmental concern for Europeans after climate change.<sup>1</sup> The presence of potentially toxic elements (PTEs) in the air is highly variable in time and space, thus, the challenge is to establish an extensive network of measurement sites identifying the pollution level. Despite the evident progress in the development of devices for air quality measurements, both stationary and mobile, still technical maintenance, energy

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supply and potential vandalism represent disadvantages of instrumental monitoring systems. The alternative lays in the use of natural systems (organisms) as indicators/monitors of pollution changes in the environment.<sup>2</sup> The use of mosses for the assessment of PTEs in atmospheric deposition has been studied due to their morpho-physiological features orienting mosses to air as nutritional media,<sup>3</sup> thus, hypothetically, reflecting the content of the surrounding air within the moss tissue. This premise has been investigated in numerous studies, which has led to systematic application of mosses in PTE (bio)monitoring across Europe and beyond, within the framework of the UNECE ICP Vegetation surveys on Effects of Air Pollution on Natural Vegetation and Crops.<sup>4</sup> This monitoring program has been performed every five years aiming to detect the spatio-temporal distribution of agreed PTEs (Al, As, Cd, Cr, Cu, Fe, Hg, Ni, Pb, Sb, V and Zn) in atmospheric deposits leading to pollution source detection.

Serbia has participated in the ICP Vegetation since 2000. Due to consistency in the sample pretreatment and analytical techniques, used the aim of this study was an evaluation of the PTE spatio-temporal distribution, in the moss samples collected over Serbia during the two last surveys, performed in 2015 and 2020. In addition, the assessment of factors affecting the PTE content in the moss and their ecological implications indices was performed.

## EXPERIMENTAL

### *Study area*

Details related to the study area, sampling and sample preparation<sup>5-9</sup> are given in the Supplementary material to this paper.

### *Chemical analysis*

In the laboratory, after removal of soil and plant debris, the moss subsamples per sampling site were homogenized in the unique one, which was analyzed in triplicate. The mineralization of the 0.5 g of the samples was performed by the solution of 7 mL HNO<sub>3</sub> (65 %, Sigma–Aldrich, puriss. p.a.) and 1 mL H<sub>2</sub>O<sub>2</sub> (30 %, Sigma–Aldrich, puriss. p.a.) in a microwave (Ethos 1, advanced microwave digestion system, Milestone, Italy) for 45 min at 200 °C. The digested samples were diluted with distilled water up to a volume of 50 mL.

The concentrations of Al, As, Cd, Cr, Cu, Fe, Ni, Pb, V and Zn were determined from the solution, using inductively coupled plasma-optical emission spectrometry (ICP-OES, Thermo Scientific iCAP 6500 Duo, Thermo Scientific, UK) and inductively coupled plasma-mass spectrometry (ICP-MS, Thermo Scientific iCAP Q, Thermo Scientific, UK). For the calibration of ICP-OES and ICP-MS a multi-element plasma standard solution 4, Specpure (Alfa Aesar GmbH & Co KG, Germany) was used to prepare intermediate solutions. The measurements were corrected to analytical blanks, and the quality control was performed by analysing certified reference materials M2 and M3 (moss *P. schreberi* (Brid.) Mitt., Finnish Forest Research Institute).<sup>10</sup> The recovery of the elements was in the range of 86–109 % and 87–107 % for M2 and M3, respectively, except for Cr (≈70 %), which was below the lower ranges for surveys in 2015 and 2020, and Ni (≈140 %) above the higher values of the range in 2020. Hence, in the following discussion, Cr and Ni will be considered with caution.

### Data analysis

The obtained results were analysed using software Statistica 8.0 (StatSoft Inc., Tulsa, OK, USA) and ArcGIS 10.4 (ESRI). All the statistical analyses were performed at a confidence level of  $p < 0.05$ . The normality of the data distribution was tested by the Kolmogorov–Smirnov test. Background values of element concentrations, in the moss samples for the study area, were estimated as 10 percentiles of element concentrations found in all the samples. In addition, the moss PTE concentrations, from this study, were compared with “fingerprint moss” (FM) values of elemental concentrations in two moss species: *Hylocomium splendens* and *Pleurozium schreberi*, which is assumed as a typical moss PTE value in remote areas.<sup>11</sup>

Enrichment factor ( $EF$ ) is a widely used metric for determining how much the presence of an element in a sampling medium has increased, relative to average natural abundance in the Earth's crust or topsoil, due to anthropogenic influence. The element  $EF$ s in the moss samples was calculated, with respect to their average crustal content,<sup>12</sup> according to the following equation:<sup>13</sup>

$$EF = \frac{(C_x / C_{ref})_{Moss}}{(C_x / C_{ref})_{E. crust}} \quad (1)$$

where  $C_x$  represents the moss element concentration and  $C_{ref}$  is the concentration of the reference element (Al) in the relevant background (e.g., the Earth's crust). According to some theoretical assumptions, if  $EF$  is close to unity, then crustal material is likely to be the predominant source of the element, while the more  $EF$  exceeds unity the higher are contributions from non-crustal sources.<sup>14,15</sup> A finer scaling of  $EF$ s is given in Aničić Urošević *et al.* (2018).<sup>16</sup>

Geo-accumulation index ( $I_{geo}$ ) is defined by the following equation:<sup>17</sup>

$$I_{geo} = \log(2 \times 1.5 C_i C_{Ti}) \quad (2)$$

where  $C_i$  represents the sample element concentration and  $C_{Ti}$  is the background or reference value for element  $i$ . In this study, background values of  $C_{Ti}$  in the moss samples were estimated as 10 percentiles of element concentrations found in all the samples over the study area. The constant 1.5 in Eq. (2) is the background matrix correction factor due to variability. The classification for  $I_{geo}$ <sup>17,18</sup> is given in Aničić Urošević *et al.* (2018).<sup>16</sup>

Contamination factors ( $CF$ s) were calculated to assess the contamination level of the study area, *i.e.*, the increment levels of an element along sampling sites due to human activity according to equation:<sup>19</sup>

$$CF = C_{element} / C_{background} \quad (3)$$

Pollution load index ( $PLI$ ), as a measure of cumulative pollution of the measured pollutants,<sup>20</sup> was calculated for the moss samples as the  $n^{\text{th}}$  root of  $n$   $CF$ s:

$$PLI = (CF_1 \times CF_2 \times CF_3 \times \dots \times CF_n)^{1/n} \quad (4)$$

where  $n$  represents the total number of measured PTEs. The values of  $PLI$  are indicative of the overall level of pollution caused by the measured pollutant and scaled.<sup>21</sup>

## RESULTS AND DISCUSSION

*Spatio-temporal trend of PTE concentration in moss samples over the investigated area*

In this study, due to the relevance of comparison, the data related to the overlapping sampling sites (177 in all) at the territory of Serbia outside of Kosovo and Metohija province in two consecutive surveys, 2015 vs. 2020, were compared.

Descriptive statistics of concentrations of ten elements, determined in moss *H. cupressiforme* samples are presented in Table I. Analysed elements are defined as important for monitoring due to their harmful effects on crops and (semi)-natural vegetation.<sup>4</sup> The PTEs in moss samples collected across the investigated area were normally or log-normally distributed depending on the element. The data characterized moderate to high values of coefficient of variation (429 % >  $CV > 53$  %), skewness (2–13) and kurtosis (6–173), thus indicating high variability of the element concentrations in the moss samples across the study area.

TABLE I. Descriptive statistics for element concentrations (mg kg<sup>-1</sup>) in the moss samples of *H. cupressiforme* collected in the surveys performed in 2015 (grey rows) and 2020; number of overlapping sites, ( $N$ )=177; fingerprint mosses: FM1 – *H. splendens* and FM2 – *P. schreberi*<sup>11</sup>

| Year | Element | Mean   | Median | Min    | Max   | 10 %  | <i>SD</i> | <i>CV</i> | Skew | Kurt | FM1  | FM2 |
|------|---------|--------|--------|--------|-------|-------|-----------|-----------|------|------|------|-----|
| 2015 | Al      | 1247   | 990    | 358    | 11000 | 573   | 1027      | 82        | 5    | 44   | 322  | –   |
| 2020 | Al      | 1833   | 1148   | 162    | 12356 | 432   | 1970      | 107       | 2    | 7    |      |     |
| 2015 | As      | 1.186  | 0.695  | 0.164  | 71    | 0.376 | 5.07      | 428       | 14   | 190  | –    | 0.2 |
| 2020 | As      | 0.952  | 0.808  | 0.0112 | 5     | 0.155 | 0.71      | 75        | 2    | 6    |      |     |
| 2015 | Cd      | 0.207  | 0.180  | 0.050  | 0.93  | 0.120 | 0.11      | 55        | 3    | 13   | 0.3  | 0.2 |
| 2020 | Cd      | 0.302  | 0.224  | 0.0082 | 1.51  | 0.139 | 0.24      | 81        | 3    | 9    |      |     |
| 2015 | Cr      | 3.739  | 2.908  | 0.006  | 25    | 0.006 | 3.90      | 104       | 2    | 7    | 1.07 | 0.9 |
| 2020 | Cr      | 3.006  | 2.128  | 0.0014 | 23    | 0.718 | 3.28      | 109       | 3    | 13   |      |     |
| 2015 | Cu      | 12.101 | 8.275  | 3.247  | 213   | 5.107 | 18        | 151       | 8    | 78   | 4.9  | 4.5 |
| 2020 | Cu      | 9.947  | 5.393  | 0.002  | 121   | 0.815 | 14        | 141       | 4    | 26   |      |     |
| 2015 | Fe      | 1275   | 995    | 275    | 10119 | 564   | 1024      | 80        | 4    | 31   | 210  | 150 |
| 2020 | Fe      | 1033   | 814    | 0.0021 | 9913  | 201   | 1056      | 102       | 4    | 29   |      |     |
| 2015 | Ni      | 4.189  | 2.868  | 0.621  | 49    | 1.532 | 5.39      | 129       | 6    | 46   | 1.4  | 0.6 |
| 2020 | Ni      | 1.999  | 0.039  | 0.0075 | 24    | 0.013 | 4.14      | 207       | 3    | 11   |      |     |
| 2015 | Pb      | 5.141  | 3.969  | 0.363  | 30    | 1.620 | 4.38      | 85        | 3    | 11   | 9.1  | 5.9 |
| 2020 | Pb      | 4.183  | 3.900  | 0.0023 | 18    | 1.823 | 2.44      | 58        | 2    | 8    |      |     |
| 2015 | V       | 3.083  | 2.649  | 0.907  | 21    | 1.454 | 2.13      | 69        | 5    | 32   | 1.75 | 1.4 |
| 2020 | V       | 3.622  | 2.584  | 0.0085 | 22    | 1.238 | 3.12      | 86        | 2    | 8    |      |     |
| 2015 | Zn      | 24     | 21     | 8      | 115   | 13    | 15        | 60        | 4    | 18   | 26.5 | 25  |
| 2020 | Zn      | 12     | 10     | 4      | 87    | 6     | 9         | 76        | 5    | 35   |      |     |

High positive values of skewness and kurtosis indicate the data are skewed positively with a tendency to maximum values, which characterized the lognormal distribution model and environmental data in general.<sup>22</sup> Although the

samples were collected in remote areas, high spatial variability of data is likely linked to the impacts of anthropogenic sources as well as geogenic and meteorological conditions on the sampling sites. In both surveys 2015 and 2020, the median PTE concentrations kept the similar order of abundance (Fe > Al > Zn > Cu > Pb > Cr > Ni > V > As > Cd, 2015; Al > Fe > Zn > Cu > Pb > V > Cr > As > Cd > Ni, 2020) in the moss tissue (Table I).

Comparing the results of 2020 and 2015 moss sampling campaigns, the median concentrations of the elements follow a decreasing pattern for Cr (41.6 %), Cu (39.4 %), Fe (21.7 %), Pb (9.5 %) and Zn (53.6 %), increasing for Cd (18.4 %), while staying about the same level for As and V. In general, these results follow the findings relevant for most EU countries participating in the program about the clear decreasing trend of the element concentrations with time.<sup>23</sup> The only element that did not follow the European time-trend of the PTE concentrations was Cd, which kept the stable or slightly increased concentrations in the investigated part of Serbia throughout the surveys performed.

Since descriptive statistics hide details about the distribution of the PTEs across the investigated terrain, the maps of the spatio-temporal element distribution in 2015 and 2020 surveys are presented in Figs. 1 and 2.

Arsenic is an element whose concentration in the moss samples increased with time at some studied sites situated in Vojvodina, the northern province of the country, and at the particular sites within the central and southeast parts of the country as well, while the decrease in concentration was observed at the particular sites within the southwest and central part of the country (Fig. 1). Contrary, at the European level, the concentration of As in the mosses have declined by 13 % since year 1995, when the biomonitoring program started.<sup>23,24</sup> It should be noted that high background values of As characterize the central Balkan peninsula and come from specific geological formations and ore deposits.<sup>25</sup> This peculiarity may cause an important contribution of this element in any environmental samples, *e.g.*, sediments and groundwater within the Pannonian Basin<sup>26</sup> or even drinking water,<sup>27</sup> birch and linden samples.<sup>28</sup> Other sources of As include anthropogenic activities, such as the application of pesticides and mineral fertilizers, fossil fuel combustions, mining activities, and disposal of industrial wastes.<sup>29</sup> In the investigated area, anthropogenically emitted As probably comes from pyrometallurgical processes of copper recovery from the sulfide mineral arsenopyrite (FeAsS) in Bor's region,<sup>30</sup> and from coal combustion in coal-fuelled power plants (the sites along such plants, located in Obrenovac, Kostolac, Lazar-evac and Svilajnac).

Cadmium is an element whose spatial distribution is rather uniform throughout the study area, with an increase of concentrations across Vojvodina province in the 2020 moss survey and with some hot spots distributed evenly throughout the country, especially in the later survey (Fig. 1). A possible source of Cd are

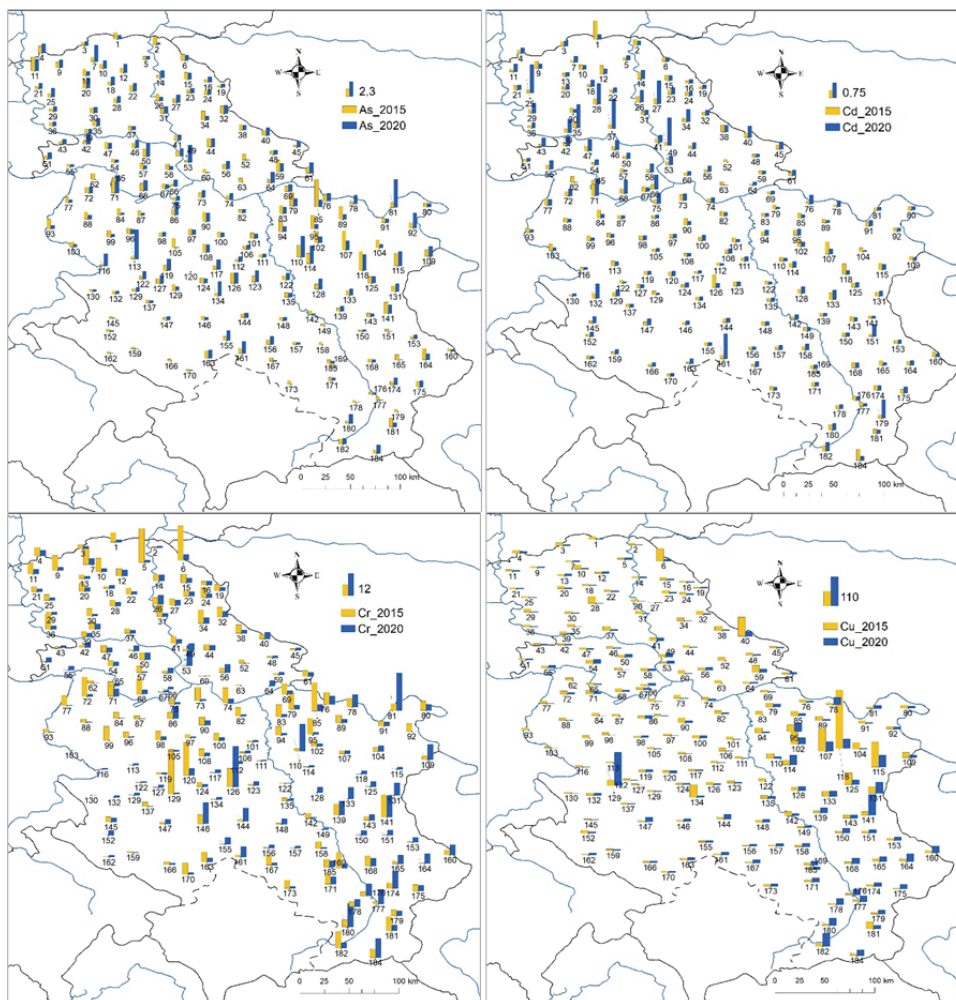


Fig. 1. Concentrations ( $\text{mg kg}^{-1}$ ) of As, Cd, Cr and Cu in the samples of moss *H. cupressiforme* in two moss surveys, 2015 and 2020.

phosphate fertilizers<sup>31</sup> with characteristic applications in the agricultural province in the north of the country. Naturally, Cd is a crustal element found in igneous and sedimentary rocks, with an average content of  $0.41 \text{ mg kg}^{-1}$  in soil worldwide and a substantially higher coal content ( $0.5\text{--}170 \text{ mg kg}^{-1}$ ).<sup>32</sup> Although at the European level, this element records a strong drop in concentration over time (63 %),<sup>23</sup> in the investigated part of Serbia, the median Cd recorded an increase over the years of investigations.

Chromium is an element with uneven spatial distribution in moss samples across the investigated part of Serbia. Having natural origin in parent (basaltic) rocks, Cr is released to the air primarily by coal mining and combustion pro-



cesses,<sup>33,34</sup> but also by cement factories and the metal processing industry.<sup>35</sup> The concentration of chromium decreased (24 %) in the moss samples of other European countries,<sup>23,24</sup> and the same trend was also recorded in this study.

Copper is an element with a prominent concentration in the moss samples collected across the eastern part of the country with the active copper mining and processing industry,<sup>30</sup> and particular sites in the west Serbia close to Copper Rolling Mill "Sevojno". In the areas with intensive agricultural production, there are several sites with an increased level of Cu (*e.g.*, Vršac vineyards), fully in accordance with the history of long-term application of mineral fertilizers and fungicides.<sup>36</sup> Still, the concentrations of Cu in the mosses decrease through the years to the median level of 5.4 mg kg<sup>-1</sup> in the last survey (2020), having the same pattern as the geometric mean of the same element in European countries,<sup>24</sup> which since 1990 has declined by 30 %.

Nickel is evenly distributed (Fig. 2) in the moss samples collected over investigated part of Serbia, probably due to numerous anthropogenic usages of this widely used ferromagnetic metal, such as production of stainless steel and alloys and corrosion-resistant plating. It is also being extensively emitted in oil combustion processes.<sup>37</sup> This element also showed a declining trend of concentrations in the moss samples with time.

Lead is an element evenly distributed (Fig. 2) in moss samples across investigated part of Serbia. Possible historical pollution of soil by deposition of lead gasoline combustion products and their resuspension processes can contribute to the relatively high presence of Pb in the environment. Still, Pb showed a decline in the concentration levels in two last moss surveys for about 10 %. This element showed the highest decline of the moss concentration since 1990, for 82 % over the Europe.<sup>23</sup>

Vanadium is an element with the highest presence in the moss samples collected across the eastern part of the country (Fig. 2), somewhat less in the moss of the northern province of Vojvodina, while the content in moss samples across the western and central parts of the country was the lowest.

Despite the V concentrations substantially decreasing with time (for 57 %) at the European level,<sup>23</sup> in the Serbian moss samples, the median element concentrations remain at the same level in the two last surveys. Releases of V to the environment are mainly associated with industrial sources, especially oil refineries and power plants using fuel oil and coal.<sup>38</sup>

Zinc is an element evenly distributed in the moss samples over the investigated part of Serbia (Fig. 2), with markedly increase concentrations at some sites in western Serbia (close to Copper Rolling Mill "Sevojno") which is also found in the stream and river water in this region.<sup>39</sup> The element concentrations showed a substantial decrease in the two consecutive surveys over the inves-

tigated area, which is in accordance with the decrease of its content at the European level (for 23 %).<sup>23</sup>

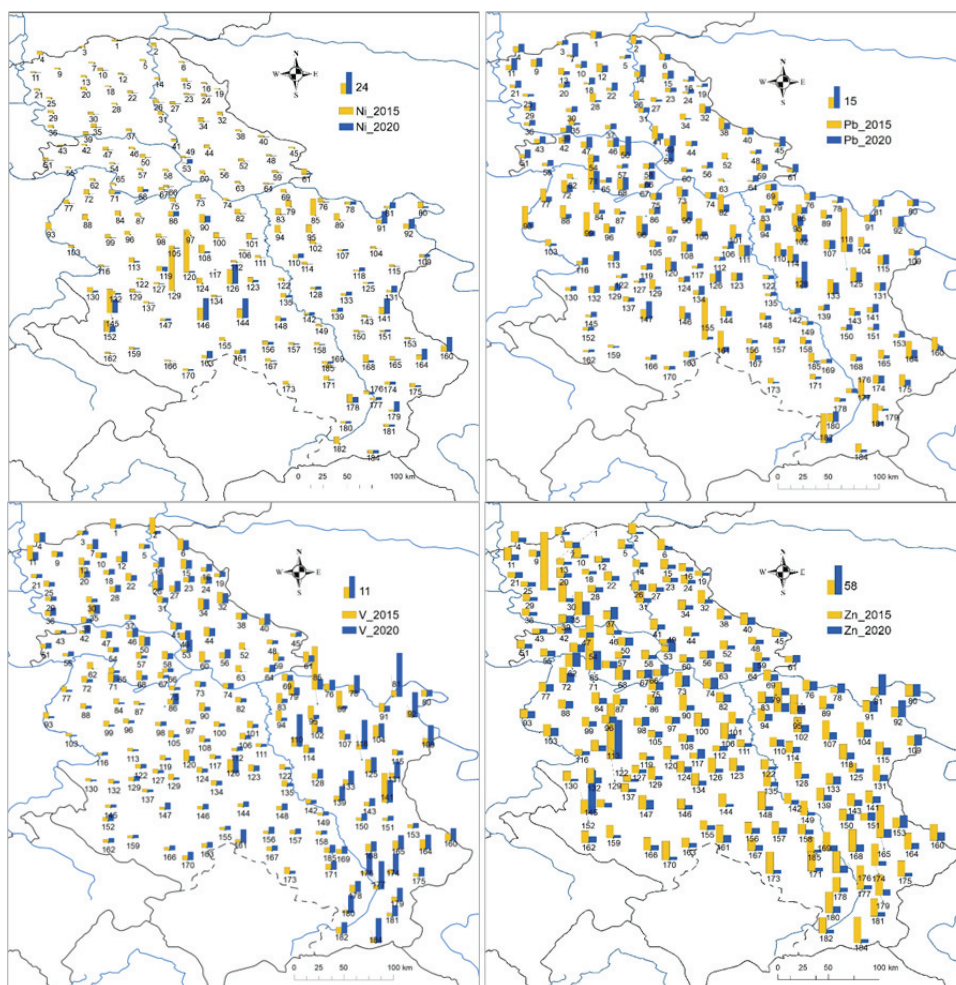


Fig. 2. Concentrations ( $\text{mg kg}^{-1}$ ) of Ni, Pb, V and Zn in the samples of moss *H. cupressiforme* in two moss surveys, 2015 and 2020.

#### *Ecological implications indices*

Calculating various ecological indices helps to put the absolute values of the PTEs determined in the studied samples into the context of environmental pollution, while scaling the contamination level of the studied moss samples allows the comparison of data from different regions.

*Enrichment factor (EF)*. In the 2015 moss survey, the median  $EF_{E,\text{crust}}$  is indication of elemental contamination levels that range from extremely severe for



Cd (73), over very severe for As (29), and severe for Zn (23), Pb (22) and Cu (12), to moderate for Ni (3), and minor for Cr (1.8), Fe (1.7), and V (1.5), Fig. 3. Five years later, in the 2020 moss survey, the PTEs kept the same range of enrichment for Cd (83), As (33), Pb (23), Zn (12), V (1.4), and Cr (1.3), while Cu (8.7), Fe (0.6) and Ni (0.5) moved to the lower category of enrichment.

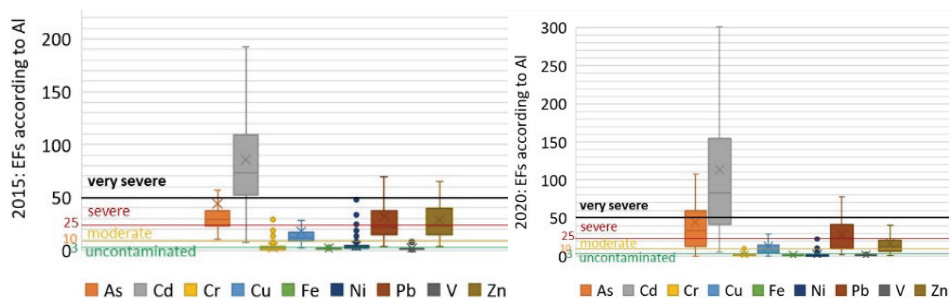


Fig. 3. Enrichment factors ( $EFs$ ) calculated for the element concentrations in the moss samples collected over the investigated part of Serbia in 2015 and 2020 with classification of contamination levels.

Searching for contamination levels of elements originating from non-natural sources, the PTE concentrations in the studied moss samples were compared with FM values assumed as the background elemental concentrations for mosses.<sup>11</sup> Median concentrations of Al, As, Cr, Cu, Fe and V in this study were elevated compared to the FM values, while Zn in both surveys, and Cd in 2015 and Ni in 2020, were below the FM values; Pb was the only element that was below the FM values in both surveys (Table I).

However, minimal PTE values in *H. cupressiforme* obtained for the study area were far below the FM values, especially for Pb. It should be emphasized that FM values are related to different moss species (*H. splendens* and *P. schreberii*) recommended for use within the ICP Vegetation program as well as *H. cupressiforme* used in this study. Some studies pointed out that comparative use of different species within the same survey could lead to wrong conclusions.<sup>40,41</sup> Thus, in further estimations of environmental indices through different pollution indexes ( $I_{geo}$ ,  $PLI$ ), the PTE background values were specifically estimated for the investigated part of Serbia as 10 percentiles of the concentrations found in all the samples.

**Geo-accumulation index ( $I_{geo}$ ).** In the 2015 moss survey, the median values of  $I_{geo}$  in the moss samples suggested the contamination by the PTEs over the investigated area in the range from uncontaminated to moderately contaminated ( $0 < I_{geo} < 1$ ), Fig. 4.

However, there are particular sites that are characterized as extremely contaminated by As and Cr (6.9 and 5.07 at sites 120 and 129, respectively); strongly

to extremely by Cu and Ni (4.8 and 4.3 at sites 118 and 120, respectively); strongly by Pb, Fe and V (3.6, 3.6, and 3.3 at sites 118, 85, and 85, respectively); and moderately to strongly by Zn and Cd (2.5 and 2.3 for site 1, Fig. 3). In the 2020 moss survey, median  $I_{geo}$  also implied slight contamination for most PTEs over the study area except for Cu (2.1) and Fe (1.4), which testified about moderate contamination. Again, for some sites, values of  $I_{geo}$  showed up to extreme contamination for Ni (up to 10 at dozen sites) and Cu (up to 6.6 at sites 133, 67, 116, 117, 184); strong to extreme for Fe (5.0 at site 81), Cr (up to 4.4 at sites 81 and 126), As (up to 4.3 at sites 113 and 81); strong for V (up to 3.5 at site 81 and 110) and Zn (up to 3.2 at sites 153 and 130); and moderate to strong for Cd (up to 2.9 at sites 37, 25, 27, 28) and Pb (up to 2.7 at sites 128, 148 and 71).

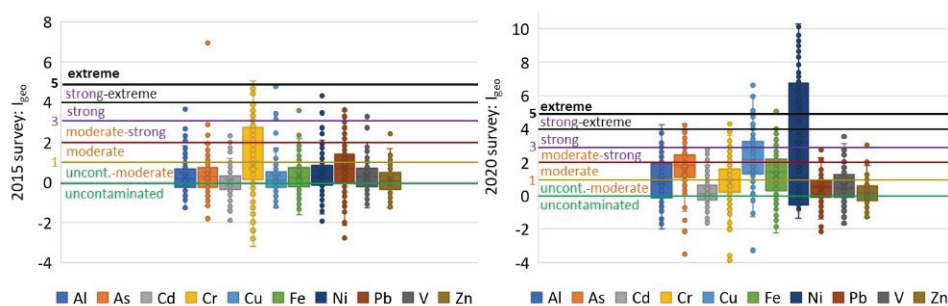


Fig. 4. Geo-accumulation index ( $I_{geo}$ ) calculated for the element concentrations in the moss samples collected over the investigated part of Serbia in 2015 and 2020 with classification of contamination levels.

**Pollution load index (PLI).** In 2015, the median  $PLI$  (1.23) for the PTEs in the moss samples over the investigated part of Serbia suggested that the area is mostly uncontaminated to moderately contaminated (Fig. 5). However, several sites reached the range of moderately contaminated ( $2 < PLI < 3$ ). Regarding the 2020 survey, the median  $PLI$  stayed in the same range as in the previous survey, but with an increasing number of sites reaching the range of moderately contaminated.

#### *Regional distribution of moss PTE content*

The PTE content in the moss samples collected over the investigated part of Serbia in 2015 and 2020 was compared with the moss PTE content in the corresponding studies of the neighboring countries (Romania, Bulgaria, North Macedonia and Albania), and the countries with low levels of environmental pollution such as Switzerland and Norway (Table II). Substantially higher PTE concentrations were found in the moss collected over Balkan countries compared to the corresponding background countries, especially of As, Cr and Pb (5–10, 3–15, 2–6 fold higher, respectively); and with somewhat less extent of Cd, V and Cu

(1.5–3, 2–3.5, about 2 times higher, respectively). Regarding Serbia, the difference in the moss element content compared to Norway was always close to the lower border of the abovementioned ranges. The peculiarity represented the As concentrations in the investigated part of Serbia, which were twice as high as in the neighboring countries, except for Romania, which is probably linked to the geological presence of this element combined with strong anthropogenic sources such as pyrometallurgical processes of copper recovery from the mineral arsenopyrite in the Bor region<sup>30</sup> and combustion in coal-fired power plants (“Nikola Tesla”, “Kolubara” and “Kostolac”).<sup>34</sup> Based on moss biomonitoring observations at the European level, the evaluated region is a factor ten, or higher, than in other parts of Europe.<sup>23,24</sup>

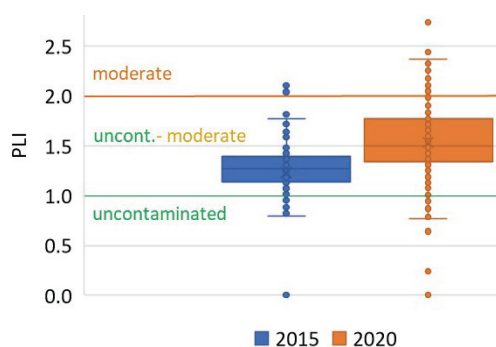


Fig. 5. Cumulative pollution (pollution load index, *PLI*) by ten PTEs in the moss samples collected over the investigated part of Serbia in 2015 and 2020.

TABLE II. Median concentrations of the PTEs in moss *H. cupressiforme* collected over the investigated part of Serbia (SRB), Albania (ALB), North Macedonia (MKD), Bulgaria (BGR), Romania (ROU), Switzerland (CHE) and Norway (NOR) in 2015 and 2020 surveys

| Element | 2015                  |                                    |                                    |                                     |                                     |                                    |                                     | 2020                  |                                    |                                    |
|---------|-----------------------|------------------------------------|------------------------------------|-------------------------------------|-------------------------------------|------------------------------------|-------------------------------------|-----------------------|------------------------------------|------------------------------------|
|         | SRB<br><i>n</i> = 177 | ALB <sup>23</sup><br><i>n</i> = 55 | MKD <sup>23</sup><br><i>n</i> = 72 | BGR <sup>23</sup><br><i>n</i> = 115 | ROU <sup>23</sup><br><i>n</i> = 214 | CHE <sup>23</sup><br><i>n</i> = 73 | NOR <sup>23</sup><br><i>n</i> = 464 | SRB<br><i>n</i> = 177 | ALB <sup>42</sup><br><i>n</i> = 55 | MKD <sup>43</sup><br><i>n</i> = 72 |
| Al      | 990                   | 1521                               | 2100                               | 2310                                | 2895                                | 318                                | 461                                 | 1148                  | 1240                               | 500                                |
| As      | 0.70                  | 0.42                               | 0.54                               | 0.45                                | 1.08                                | 0.14                               | 0.13                                | 0.81                  | 0.36                               | –                                  |
| Cd      | 0.18                  | 0.12                               | 0.23                               | 0.10                                | 0.27                                | 0.12                               | 0.08                                | 0.22                  | 0.10                               | 0.15                               |
| Cr      | 2.9                   | 9.3                                | 5.7                                | 2.73                                | 4.72                                | 0.85                               | 0.66                                | 2.1                   | 6.2                                | 3.5                                |
| Cu      | 8.3                   | 10                                 | 4.6                                | 7.4                                 | 5.8                                 | 4.8                                | 4.2                                 | 5.4                   | 4.7                                | 6.3                                |
| Fe      | 995                   | 1735                               | 1700                               | 1190                                | 1533                                | 314                                | 310                                 | 814                   | 1444                               | 620                                |
| Ni      | 2.9                   | 7.6                                | 3.5                                | 2.1                                 | 3.11                                | 1.12                               | 1.2                                 | 0.04                  | 8.6                                | 2.3                                |
| Pb      | 4.0                   | 2.4                                | 4.9                                | 10.7                                | 4.2                                 | 2.13                               | 1.6                                 | 3.9                   | 3.5                                | 2                                  |
| V       | 2.6                   | 3.3                                | 3.3                                | 3.9                                 | 4.32                                | 1.05                               | 1.2                                 | 2.6                   | 3.2                                | –                                  |
| Zn      | 21                    | 18                                 | 30                                 | 28                                  | 40                                  | 27                                 | 31                                  | 10                    | 16                                 | 21                                 |

It should be noted that the same moss species (*H. cupressiforme*) were sampled in the countries of the region while different moss species were collected in Switzerland (*H. cupressiforme* and *P. schreberi*) and Norway (*H. splendens* and *P. schreberi*) thus possibly influencing the comparison of the

results. In addition, in most countries, destructive analytical techniques were used for element determination (ICP-OES, ICP-MS), except in Bulgaria and Romania, where nondestructive INNA was used. These analytical techniques require different sample pre-treatment, non-destructive and destructive, respectively, which can influence the total element content measured.<sup>44</sup>

#### CONCLUSION

Moss *H. cupressiforme* was used for the biomonitoring of PTEs, at about 200 sites across remote areas in the investigated part of Serbia, following the international Moss survey protocol. Comparison of results in the last two surveys (2015 and 2020), showed a decline in the median deposition of Cr (42 %), Cu (39 %), Fe (22 %), Pb (10 %) and Zn (54 %), an increase of Cd (18 %), and similar deposition of As and V. Concerning the average element content in the Earth's crust (*EF*), severe anthropogenic pollution input was found for As, Cd, Pb and V. However, compared to the background values of the elements in the moss ( $I_{geo}$ ), the highest indices (strong) were assessed for Cr (in 2015), and As, Cu and Ni (in 2020). Still, the cumulative measure of pollution (*PLI*) indicates that the study area suffers from moderate pollution by the measured elements. The critical points of a moss survey are strictly following the manual, using one moss species, and properly assessing the background concentration of the pollutant in the moss.

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#### ИЗВОД

#### БИОМОНИТОРИНГ АТМОСФЕРСКЕ ДЕПОЗИЦИЈЕ ПОТЕНЦИЈАЛНО ТОКСИЧНИХ ЕЛЕМЕНАТА НА ТЕРИТОРИЈИ СРБИЈЕ КОРИШЋЕЊЕМ МАХОВИНЕ: 2015. vs. 2020. ГОДИНА

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У оквиру *ICP Vegetation* програма, почевши од 2000. год., сваких 5 година се спроводи биомониторинг потенцијално токсичних елемената у неурбаним подручјима на територији Србије, коришћењем маховина (врста *Hypnum cupressiforme*). Због конзистентне методологије и анализе, у овој студији су приказани резултати два последња истраживања: 2015. vs. 2020. год. Резултати истраживања су указали на опадање концентрације Cr (42 %), Cu (39 %), Fe (22 %), Pb (10 %) и

Zn (54 %); As и V остали на истом нивоу, док је дошло до повећања концентрације Cd (18 %). Концентрације елемената у маховини су биле упоредиве са оним измереним у суседним земљама, док су медијана вредности биле пет и више пута веће од вредности измерених у маховини тзв. чистих земаља – Швајцарске и Норвешке. Израчунавањем различитих индекса еколошких утицаја закључује се да постоји ниско до умерено загађење на подручју Србије. Ипак, за поједине локалитете у источној Србији, као и Војводини, озбиљан ниво загађења је процењен за As, Cr, Cu и Pb.

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