Assessment of Atmospheric Pollution by Selected Elements and PAHs during 12-Month Active Biomonitoring of Terrestrial Mosses

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Abstract: Biomonitoring studies are most often used in short-term study periods to quickly obtain information on the state/quality of the environment and its pollution levels. Performing long-term surveys involves a prolonged wait for the result and is therefore not often used and is rather associated with classical air quality monitoring. The aim of this study was to evaluate atmospheric air pollution by selecting 16 elements and 16 polycyclic aromatic hydrocarbons conducted as part of a 12-month ‘moss-bag’ technique of an active biomonitoring method with the use of three moss species: Pleurozium schreberi, Sphagnum fallax, and Dicranum polysetum. All analytes were determined by inductively coupled plasma mass spectrometry (ICP-MS) and gas chromatography–mass spectrometry (GC-MS). As a result of the experiment, it was found that the concentrations of all elements increased with time of exposure. The total sum of them in D. polysetum moss was 30% and 60% more than in P. schreberi and S. fallax, respectively, which allows us to consider this species’ broader use in active biomonitoring. For PAHs analysis, the best biomonitor in time was P. schreberi, which accumulated 25% and 55% more than S. fallax and D. polysetum, respectively. In this one-year study, most organic compounds accumulated between 5 and 6 months of exposure, depending on the species. Given the low-cost nature of active biomonitoring, it should be concluded that mosses could be used in long-term monitoring of the quality of the atmospheric aerosol in terms of element and organic compound concentration in air.

Keywords: air quality; biological indicator; environmental monitoring; metals; organic compounds

1. Introduction

Atmospheric air pollution is still an ongoing and global problem [1,2]. Therefore, it is not surprising to see calls for its repair using all available tools [3]. This is so much more relevant as these pollutants negatively affect the health of all living creatures in general [4,5]. As recent studies have shown, despite significant reductions in some emissions (e.g., sulfur oxides, particulate matters [PM] < 10 µm), the European urban population was exposed to PM2.5 and O3 on levels widely exceeding the WHO limit values for the protection of human health [6]. The impact of air pollution along with the COVID-19 pandemic and its effect on mortality changes are also not insignificant [7–9]. However, some studies show a different trend: a reduction in air pollution resulting from maintaining social restrictions during the pandemic [10,11]. However, this does not change the fact that research and monitoring measurements of air pollution should be carried out along with source determination [12,13], including multi-year analyses [14]. The approaches in this regard used in the literature vary: low-cost air pollution monitoring systems [15], artificial intelligence (AI) models [16], the use of drones [17], the implementation of specific program plans [18], or the inclusion of citizen...
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2. Materials and Methods

2.1. Material

The species used for this study were moss *Pleurozium schreberi* (Willd. ex Brid.) Mitt., (Pl), *Sphagnum fallax* (H. Klinggr.) H. Klinggr (Sp), and *Dicranum polysetum* Brid. (Di). They were collected in August 2021 from forests in the Swietokrzyskie Voivodship in southeastern Poland. The mosses came from the Puszcza Swietokrzyska mesoregion, Staporkow Forest District (51°7′21.32″ N 20°30′5.90″ E). The sampling time is in line with science [19]. Of course, only selected examples are presented here against the background of classical air pollution monitoring [20,21] and its biological counterpart—air quality biomonitoring [22,23]—together with their mobile alternatives [24,25]. Among the many advantages of the application of biomonitoring (the use of living organisms—biomonitors) in the assessment of, for example, air pollution are the following: the ease and low cost of sampling, the high accumulation rate of species, their resistance to difficult conditions, the fact that biomonitors are widespread (range of occurrence/location), and hence, a large number of sampling sites or exposure sites are accessible [26–28]. Biomonitoring studies concern the measurement of various analytes and air pollutants, e.g., trace elements, polycyclic aromatic hydrocarbons, or now, microplastics [29–32].

For biomonitoring studies, there is a strong emphasis on validating study procedures and standardizing sample treatment protocols [33–36]. The exposure time of samples is also an important consideration [37,38] in active biomonitoring (moving samples from their natural habitat to a monitored/exposure environment to assess contamination). Typically, in the literature, we will encounter examples of short exposure times for samples, which is explained due to practical reasons (to keep the biomonitor’s vitality, to record a short-time, or to avoid accidental pollution) [39]. However, the vitality aspect is considered in a small number of papers [40,41], although the relevance of considering this parameter in biomonitoring and physiological studies has been demonstrated [42,43]. Nevertheless, a considerable number of studies use devitalized material [44–46].

Long-term biomonitoring tends to be the domain of studies carried out using passive techniques (taking samples from their natural environment and directly analyzing the pollutants). As an example, mention can be made of the surveys performed every 5 years within the framework of the International Cooperative Program on Effects of Air Pollution on Natural Vegetation and Crops in the framework of the European convention on long-range transboundary air pollution (UNEC ICP Vegetation) project [47] and the surveys following the protocols developed within this project [48]. Another slightly older example concerns a 3.5-year study conducted on the moss *Scleropodium purum* to assess changes in seasonality and variation in concentrations of selected elements: Al, K, Ca, Mg, Cu, Mn, Fe, Na, Hg, and Zn. On the basis of these studies, a method for assessing the annual bioconcentration of elements with two sampling periods six months apart was developed [49]. As mentioned earlier, for active biomonitoring, such long study periods (conducting long-term exposure periods) are not used. Most often, these are short periods of up to six months [50], although usually up to 12 weeks of sample exposure [51–55]. There are only a few studies describing the exposure of mosses over a longer period [37,56]. Another example involving long-term active biomonitoring was conducted over 16 years, where each year, bags were exposed three, non-consecutives times for 9 weeks. Analysis of the data demonstrated that moss bags are able to register environmental episodes that occurred during the biomonitoring study, and that accumulation values are affected by different ecological factors [57]. Given this introduction, we undertook a 12-month active biomonitoring study using three terrestrial moss species in an urban area to assess the air pollution of selected elements and polycyclic aromatic hydrocarbons.

The aims of this study were as follows: (i) to determine the accumulation properties of three terrestrial mosses during annual exposure (‘moss-bag’ technique) in relation to selected metals and organic compounds and (ii) identify the source of pollutants in urbanized areas.
the protocols adopted in the literature \[58,59\]. Only the green part of the gametophytes was selected for chemical analysis \[60,61\]. The mosses were collected in accordance with national regulations which limit the collection of mosses to a few species \[62\]. Moss samples were also collected in accordance with the guideline of ICP Vegetation protocols: away from tree canopy cover, roads, or any anthropogenic activity \[59\]. Control samples, which were also collected but not exposed, were set aside separately. Mosses have already been collected from these sites for biomonitoring studies on PAH determination \[63,64\]. Another criterion for selecting these species was previous testing on them in another area \[65\].

2.2. Study Area and Climate Conditions

The mosses were exposed in Końskie city (51°10′53″ N, 20°25′26″ E). This is a town in south-central Poland situated in the Świętokrzyskie Voivodeship (50 km northwest of the Voivodship city of Kielce). The warm season lasts from May to September, with the average daily maximum temperature then exceeding 19 °C. The hottest month of the year in Końskie is July, when the average maximum temperature is 23 °C and the minimum temperature is 13 °C. The cold season lasts from November to March, with an average daily maximum temperature below 5 °C. The coldest month of the year in Końskie is January, when the average minimum temperature is –5 °C and the maximum temperature is 0 °C. Rainfall occurs in Końskie throughout the year. The rainiest month in Konskie is July, when the average rainfall is 61 mm. The least rainy month in Konskie is February, when the average rainfall is 13 mm. The total annual precipitation is around 400 mm \[66\]. This district city is urbanistically similar to many other cities of its kind (ca. 18,000 inhabitants). Industrial activity in the city mainly involves foundry, construction, and transport. Nowadays, the town has developed into a major trade center for small businesses \[67\]. The research was carried out in an open space/meadow. The sample exposure sites were approximately 100 m from buildings and the nearest street road. Short-term biomonitoring studies have already been conducted at this site on the comparison of outdoor and indoor pollution \[68\]. According to the latest report of the Regional Department of Environmental Monitoring in Kielce, the level of benzo(a)pyrene in PM\(_{10}\) suspended dust in Końskie city exceeds the permissible standards. The report indicates the impact of emissions related to the individual heating of buildings as the main source of exceedances \[69\].

2.3. Methods

Five grams of each moss species were packed into nylon nets and suspended in flat bags \[70\] at a height of 1.50–2.00 m from the ground for a period of 12 months (August 2021–2022). A total of 24 bags were hung up for each species separately. Two bags of each moss species were removed after each month. \(S. \text{ fallax}\) samples for the last two months were lost during the exposure period. The bags were torn open (presumably by the wind), resulting in no moss inside. The total number of samples analyzed were 144. The samples were exposed to detect different types of contamination, particularly resulting, among other things, from the heating season in Poland (October 2021–April 2022) and the non-heating period (May–September 2022).

Once all samples were collected and transported to the laboratory, the moss samples were dried at room temperature and ground in an agate mortar, then sieved through a 100-mesh sieve and finally homogenized in a mixer for 10 min. A total of 0.1 g of each dried moss sample (weight exactly) was digested by a microwave oven (model MLS mega 1200) using a mixture of H\(\text{NO}_3\)/H\(\text{2}\)O\(_2\) following EN ISO 15587-2:2002, and then, the elements were determined using ICP-MS measurement. Each moss sample was digested 3 times \[71\]. The element concentrations were determined by using a NexION® 2000 inductively coupled plasma mass spectrometer from PerkinElmer® according with DIN EN ISO 17294-2 (E 29):2004 \[72\]. An eight-point calibration curve was generated by each one of the studied elements and the linear correlation coefficient was higher than 0.9990 for all calibration curves. The accuracy and reproducibility of the results were tested by different procedures: by a one-time/year laboratory test involved in a round robin test/proficiency test; by a
laboratory performance check daily (check detector, plasma quality, and signal performance of all measurement ranges) with a certified solution from PerkinElmer; by testing the blank and control samples at the beginning and the end of the measurements; the average and the blank result interpretation are conclusions of ISO/TS 13530:2009 [73].

For polycyclic aromatic hydrocarbon determination, 0.5 g of each dried moss sample (weight exactly) was treated according with DIN 38407 (F 39): 2011-09 and determined using the gas chromatography–mass spectrometry method (DIN—German Institute for Standardization, 2011). After sample preparation, the concentrations of 16 PAHs (Naphthalene, Acenaphthylene, Acenaphthene, Fluorene, Phenanthrene, Anthracene, Fluoranthene, Pyrene, Benzo(a)anthracene, Chrysene, Benzo(b)fluoranthene Benzo(k)fluoranthene, Benzo(a)pyrene, Indeno(1,2,3-cd)pyrene, Dibeno(a,h)anthracene, and Benzo(g,h,i)perylene) were determined by using Gas Chromatograph Agilent 6890N (Agilent Technologies, Santa Clara, CA, USA) coupled with a mass spectrometer detector Agilent 5975 according with DIN EN 17503-2020-06 [74]. A nine-point calibration curve was generated by each one of the studied PAHs and the linear correlation coefficient was higher than 0.9990 for all calibration curves. The accuracy of the method and reproducibility of the results were tested by different procedures: by a one-time per year laboratory test involved in a national round robin test/proficiency test; by calibration before each measurement in order to compensate for any changes in measuring conditions during the measurement; and by (extracted) double determination of a blank value and a control sample. PAH diagnostic ratios were used to search for PAH emission sources taken from the literature [75]. The choice of elements and PAHs determined relates to compounds that were analyzed in mosses by other authors [76,77].

Microsoft Excel 2021 and Statistica (ver 13.3) software were used to process and present the data. Shapiro–Wilk's test was used to check data normality. Therefore, differences between the seasons in terms of PAH concentrations in the mosses were evaluated by Student's t-test.

3. Results

First of all, we present in Figure 1 graphs for the three moss species of their accumulation of selected elements in successive months of exposure.

As can be seen in Figure 1, for all three species, elemental concentrations increased with exposure duration. *S. fallax* samples for the last two months were lost during the exposure period; therefore, in Figure 1b, there are no last two months of exposure. For *P. schreberi* and *S. fallax*, exposure up to six months resulted in total concentrations of about 500 µg/g, where for the same period, for *D. polysetum*, the result of total elemental concentrations was threetimes higher. Depending on the species, a monotonic, cumulative series of concentrations of all determined elements can be observed until the 10th–12th month. A certain exception is the concentration of manganese, which was not determined in *P. schreberi* and in *D. polysetum* mosses only in some selected months, but not all. It can also be seen that iron, aluminum, and zinc are dominant among the 16 elements determined. These are the three elements that contribute, depending on the species (regardless of the month), 78–92% to the total. Iron is the most dominant element, with an average share of 47.1% regardless of species. Considering the contribution of individual elements by species, the mosses can be arranged in a descending series Di > Pl > Sp in terms of analyte accumulation. The results of the individual concentrations of all elements are presented in Table S1 in the Supplementary Materials.

The concentrations of selected PAHs for the three moss species by season of exposure are presented next (Figure 2). The mean concentrations of selected and analyzed PAHs for the three moss species are presented in Table S2 in the Supplementary Materials.
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Figure 1. Average concentrations of selected elements over 12 months as a sum of elements for a given month for (a) *P. schreberi*, (b) *S. fallax*, and (c) *D. polysetum* moss. The different colors correspond to the selected elements shown in the legend at the bottom of each graph. The gray line indicates the line of the series. *S. fallax* samples for the last two months were lost during the exposure period; therefore, the last two months of exposure are not shown in (b).
Figure 1. Average concentrations of selected elements over 12 months as a sum of elements for a given month for (a) *P. schreberi*, (b) *S. fallax*, and (c) *D. polysetum* moss. The different colors correspond to the selected elements shown in the legend at the bottom of each graph. The gray line indicates the line of the series. *S. fallax* samples for the last two months were lost during the exposure period; therefore, the last two months of exposure are not shown in (b).

Figure 2. Summed PAH concentrations in individual moss species by (a) season, with different letters meaning statistical differences among seasons of exposure (*p* < 0.05); (b) summed concentrations for the three species [ng/g]. Dots represent summed maximum PAH concentrations accumulated by individual moss species. Pl—*P. schreberi*, Sp—*S. fallax*, and Di—*D. polysetum*.

As shown in Figure 2a, differences can be seen in the summed PAH concentrations for the individual seasons. Statistically significant differences are marked with different letters, respectively. The highest PAH concentrations were observed in winter (fourth to sixth month of exposure; December to February). Thereafter, a decreasing trend is observed, with the least PAHs determined in summer. Differences in the structure of the contribution of individual species can also be observed, where, for example, no PAH increments were recorded in the previously mentioned summer period for the species *D. polysetum* (Figure 2a). This is also reflected in the total sum of the analyzed PAH concentrations (Figure 2b). The species *P. schreberi* accumulated the most, $\sum_{PAH} = 17,121$ ng/g, during the annual exposure. Considering the total PAH accumulation by the mosses, they can be arranged in a descending series Pl > Sp > Di. The species *P. schreberi* accumulated 25.3% and 53.8% more compared to *S. fallax* and *D. polysetum*, respectively.

Detailed results of PAH ratios are shown in Table 1.
Table 1. PAH diagnostic ratios for mosses.

<table>
<thead>
<tr>
<th>Pl</th>
<th>$\sum_{LMW}/\sum_{HMW}$</th>
<th>FL/(FL + PYR)</th>
<th>ANT/(ANT + PHE)</th>
<th>FLA/(FLA + PYR)</th>
<th>BaA/(BaA + CHR)</th>
<th>IcdP/(IcdP + BghiP)</th>
<th>BaP/BghiP</th>
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<td>0.201</td>
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<td>2</td>
<td>0.379</td>
<td>0.034</td>
<td>0.043</td>
<td>0.603</td>
<td>0.211</td>
<td>0.536</td>
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<td>0.486</td>
<td>0.596</td>
</tr>
<tr>
<td>4</td>
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<td>0.614</td>
<td>0.219</td>
<td>0.512</td>
<td>0.629</td>
</tr>
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<td>0.638</td>
<td>0.060</td>
<td>0.545</td>
<td>0.652</td>
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<td>0.643</td>
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<td>0.862</td>
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<th>ANT/(ANT + PHE)</th>
<th>FLA/(FLA + PYR)</th>
<th>BaA/(BaA + CHR)</th>
<th>IcdP/(IcdP + BghiP)</th>
<th>BaP/BghiP</th>
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<td>n.d.</td>
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<tr>
<td>Av.</td>
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<td>0.014</td>
<td>0.673</td>
<td>0.158</td>
<td>0.348</td>
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### Table 1. Cont.

<table>
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<tr>
<th>Di</th>
<th>$\sum$LMW/$\sum$HMW</th>
<th>FL/(FL + PYR)</th>
<th>ANT/(ANT + PHE)</th>
<th>FLA/(FLA + PYR)</th>
<th>BaA/(BaA + CHR)</th>
<th>IcdP/(IcdP + BghiP)</th>
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<td>0.224 n.d. n.d. 0.014 0.697 0.075 n.d. n.d.</td>
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<tr>
<td>Av.</td>
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<td></td>
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n.d.: no data—not possible to determine because PAHs were not determined or their concentration was lower than the control sample; consecutive numbers indicate consecutive months of exposure; Pl, Sp, and Di—selected moss species: *P. schreberi*, *S. fallax*, and *D. polysetum*; Av.—mean values; $\sum$LMW—sum of two and three-ring PAHs; $\sum$HMW—sum of four and five-ring PAHs according to the literature [75,78]. Bold and background color were used to highlight the average values for individual moss species.
The calculated PAH diagnostic ratios indicate different sources of pollution; however, for all mosses, considering the mean of the whole year for the ratio FLA/(FLA + PYR) > 0.5, the source could be grass, wood, or coal combustion. A detailed analysis of the results is presented in the discussion chapter below.

4. Discussion

The trend of concentrations of selected elements is consistent with our previous own study [79]. With an increased time of exposure, elemental deposition in the mosses increases, although the opposite trend can sometimes be observed, resulting, for example, from the influence of weather conditions [56]. However, it is important to take into account the nature of the accumulation, which will rather refer to the surface absorption of contaminants [80,81]. The concentrations of selected elements obtained are similar to those obtained in literature studies. As an example, an 8-month experiment in Italy can be cited, where most of the self-assessed concentrations are similar to those conducted on the moss *Hypnum cupressiforme* [82]. It is essential in this type of research to consider the moss species itself as well as the possibility of comparing the sorption properties of different species [51,83]. Mosses as biomonitors are used as point indicators of pollution sources, and the accumulation of specific elements is directly associated with the emission source [84,85]. Therefore, the presence of concentrations of elements such as Al or Fe is not surprising as indicators of air pollution in urban areas from traffic, among other sources. Iron is also an element characteristic of industry or oil burning, so its presence in the air in urban areas is fully justified [86]. A 10-week exposure period of *Sphagnum girgensohni* mosses in the vicinity of the airport indicates an average maximum concentration of this element at around 500 µg/g, whereas for our species *S. fallax*, such a concentration was only obtained after 7 months of exposure [87]. This indicates that the distance from the emitter and the specificity of the emitter significantly affects the result and the obtained concentrations of individual elements [80,88]. This is also confirmed by the determined iron concentrations, which were about 20,000 µg/g for our mosses after 11 months of exposure, whereas for half the time, moss bags with *Ceratodon purpuratus* and *Brachythecium campestre* moss species were exposed for 6 months in the surroundings of two steelworks, a power station, and two parks, and iron concentrations averaged over 54,500 and 42,500 mg/kg, respectively [89]. Another example shows much lower determined Fe concentrations, where an average of 1236 mg/kg for the Hanoi region was determined for the moss *S. girgensohni* after 2 months. The main potential sources of pollution were suggested to include soil and road dusts emitted from traffic, industrial activities, biomass burning, and the sea [90], whereas only 24 µg/g was determined for the corresponding time for our species *S. fallax*. This indicates differences in the selection of the measurement site and the influence of the site on the level of contamination [91,92]. The outcome of this study will, of course, still be influenced by the season in which the study was conducted. A literature example on *S. girgensohni* conducted in Belgrade during the winter season (December–February) shows average Al, Fe, and Zn concentrations of 530, 800, and 860 µg/g, respectively [92]. For our mosses, for the corresponding time period to that study (winter season), the mean concentrations of aluminum and iron were similar (not after 2 months, but after 4–6 months of exposure). The zinc concentration in our study for the corresponding time period was about 100–150 µg/g. Nevertheless, the influence of the heating season and related combustion processes (house heating) influences the highest concentrations of elements and PAHs in mosses [92], as reflected in our results of seasonal changes in PAHs, which are shown in Figure 2. It should be pointed out that the studied city of Końskie is not a highly polluted area as far as zinc concentrations are concerned. Despite the fact that the contribution of this element is (regardless of moss species) about 10%, its concentrations are low in relation to literature studies. Research carried out in Lithuania (Vingis Park, the largest park in Vilnius) indicates strong zinc contamination, especially when sampling the moss *Pylaisia polyantha* 5 m from the road, where the concentrations reached, depending on the period of sampling, around 300 mg/kg; the results of the study clearly indicate a strong
traffic-related gradient—the zinc concentration in moss samples tends to decrease with the
distance from the source of contamination—Geležinis Vilkas Street [93]. In comparison,
our own research conducted on three moss species (the same as in this study) indicates
that zinc concentrations in moss samples exposed next to the roadway at a distance of
approximately 5 m were 8–19 µg/g [68], indicating that intensity of use and traffic volume
will influence the final concentration result [94,95], and this demonstrates the low level of
air pollution in the study area.

As previously stated, seasonal variations can be observed in the case of PAHs, where
the summed concentration of these compounds were highest in winter (Figure 2a), which
is related to their emissions during the heating season (heating) [92]. Similar conclusions
were reached by F. Capozzi et al., who observed that a significant increase in PAHs was
measured in the moss H. cupressiforme during the winter period, especially in devitalized
compared to living material. This result suggests that PAH uptake is mainly based on
passive mechanisms [40]. Similar conclusions were also reached in the first use of Hy-
locomium splendens to measure annual variation in atmospheric PAH deposition, where
higher levels in winter were likely due to significant PAH emissions from domestic heating
and lower photodegradation of PAHs in the atmosphere [96]. Differences in the seasonal
accumulation of PAHs in moss can be caused by lower concentrations of the particle phase
in the air during summer and autumn and increased particulate concentration in winter
and spring, as observed for P. schreberi, where we find a decreasing trend from March
to October [97], which is also in line with our observations. Moss has shown a greater
tendency to capture high molecular weight PAHs [98], as evidenced by the results of our
research for individual PAHs (Table S2). However, the sorption differences between the
different species are relevant to the results obtained, because comparing the concentrations
of selected PAHs in relation to the studies in Mexico City indicates a low accumulation
capacity of the Hypnum amabile species used or a low contamination of these compounds
in the area [99]. For example, for our P. schreberi, after one month, the concentration of
pyrene was 63.7 ng/g, and for the cited example, regardless of the exposure site, it did not
exceed 9 ng/g. Differences in concentrations will not only depend on the moss species
used but also on the nature of the experiment and the method of conducting it. Different
results will be obtained by taking mosses and analyzing the concentrations of PAHs’ pas-
sive biomonitoring [100] versus the ‘moss-bag’ technique [101]. An earlier study that we
conducted confirms the usefulness of using active biomonitoring in assessing air pollution
of the provincial city of Opole by selected PAHs during the winter period [65]. The results
obtained there indicate a much higher contamination of mosses with these compounds
compared to the present study. Nevertheless, the best comparison and discussion of the
results makes sense for the same study periods. In the literature so far, only one such
study has been published on annual active biomonitoring using mosses to assess PAH
deposition in them [96]. In this research, in the year between June 2010 and May 2011, the
total concentrations of the 13 PAHs measured in the H. splendens mosses placed under the
Bertiz forest canopy varied greatly, from 129 ± 6 ng/g in June 2010 to 1059 ± 600 ng/g
in October 2010. These values differ significantly from those obtained by us in our study.
First of all, we analyzed three more PAHs, as well as the number of our samples (n = 144)
being significantly higher than the mentioned study (n = 8). In addition, the location of
the mosses in a Spanish nature reserve (a potentially low-pollution site), and moreover,
under a canopy, also influences the final result, as it has already been proven that when
mosses are exposed under a cover, the results obtained are lower than those of uncovered
mosses [68,102]. Diagnostic ratios [e.g., BaA/(BaA + CHR)] in the study cited showed that
the contamination comes mainly from car road traffic and pollutant emissions augmented
in winter by domestic heating [96]. In our study, the mean value of this ratio for the three
moss species was <0.2, which would indicate a petrogenic source. However, in winter,
for P. schreberi and S. fallax, this ratio was above 0.2, which would be associated with a
‘coal combustion’ source, which would be consistent with the exposure period and the
possibility of house heating as early as autumn. However, using this ratio together with
ANT/(ANT + PHE), which are particularly sensitive to changes, is risky [75]. It is proposed to use more conservative and safer ones such as FLA/(FLA + PYR) and IcdP/(IcdP + BghiP) [75,103]. For the first ratio in each moss, the value exceeds 0.5, i.e., the source is referred to as “grass, wood, coal combustion”, and for the latter, only for P. schreberi and S. fallax, the values vary between 0.2 and 0.5 and the source is “petroleum combustion” [75]. Regardless of the ratios used, it should be taken into account that diagnostic ratios should not be routinely used without first carefully assessing most environmental processes and their influence on the calculated values [104]. In conclusion, the individual values of the indicators obtained in our experiment are related to combustion processes, and the mosses were able to accumulate these pollutants.

5. Conclusions

Annual biomonitoring using three moss species in an urbanized area indicates the continuous, cumulative nature of the concentrations of the selected elements determined throughout the study period. The structure of the contribution of the individual analytes varied from month to month, but Al, Fe, and Zn formed the core of approximately 85% of the contribution over the others. Accumulation of these elements by mosses is related to urban pollution associated with traffic. D. polysetum moss proved to be the best biomonitor throughout the experimental cycle.

The concentrations of the PAHs analyzed, in contrast to the elements, showed seasonal variation and most of these compounds were determined in winter. The contamination of PAHs in winter represents more than 50% compared to the other seasons. The best biomonitor of these pollutants was found to be the moss P. schreberi, which confirms previous short-term studies and offers the possibility that this species can be widely used for PAH monitoring in urban environments using the ‘moss-bag’ technique. The calculated diagnostic ratios, but also the contribution of the individual compounds, indicate a pollution whose source is mainly road traffic and combustion processes (mainly in winter heating).

In the end, it should be concluded that Koškúske city is not a highly polluted town against the background of the literature examples cited, but the effectiveness of the active biomonitoring method using mosses makes it possible to determine the negative impact of anthropogenic activities on air quality in this location.

Supplementary Materials: The following supporting information can be downloaded at: https://www.mdpi.com/article/10.3390/atmos15010102/s1, Table S1: Average elemental concentrations in mosses during the one-year experiment—relative values [µg/g]; Table S2: Average concentrations of PAHs in mosses during the one-year experiment—relative values [ng/g].


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