First-Time Source Apportionment Analysis of Deposited Particulate Matter from a Moss Biomonitoring Study in Northern Greece

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Abstract: Moss biomonitoring is a widely used technique for monitoring the accumulation of trace elements in airborne pollution. A total of one hundred and five samples, mainly of the Hypnum cupressiforme Hedw. moss species, were collected from the Northern Greece during the 2015/2016 European ICP Vegetation (International Cooperative Program on Effects of Air Pollution on Natural Vegetation and Crops) moss survey, which also included samples from the metaliferous area of Skouries. They were analyzed by means of neutron activation analysis, and the elemental concentrations were determined. A positive matrix factorization (PMF) model was applied to the results obtained for source apportionment. According to the PMF model, five sources were identified: soil dust, aged sea salt, road dust, lignite power plants, and a Mn-rich source. The soil dust source contributed the most to almost all samples (46% of elemental concentrations, on average). Two areas with significant impact from anthropogenic activities were identified. In West Macedonia, the emissions from a lignite power plant complex located in the area have caused high concentrations of Ni, V, Cr, and Co. The second most impacted area was Skouries, where mining activities and vehicular traffic (probably related to the mining operations) led to high concentrations of Mn, Ni, V, Co, Sb, and Cr.

Keywords: positive matrix factorization model; trace elements; moss; biomonitoring; neutron activation analysis

1. Introduction

Trace elements are dispersed widely in all ecosystems. They interact with different natural components of the environment and they have a significant impact on the biosphere [1–3]. The majority of trace elements are deposited on the terrestrial environment from the atmosphere through either wet or dry deposition. The atmospheric deposition of trace elements is a matter of great concern worldwide, as, depending on their concentrations, trace elements may be hazardous both for humans and the environment [4–7].

In order to determine the atmospheric deposition of trace elements, complicated and expensive classical analytical methods are usually required. However, there is another reliable technique that uses living organisms (grass, leaves, pine needles, mosses, and lichens) in order to study the environmental quality and the effects of trace elements on the
biosphere [8–13]. The biomonitoring technique is a rapid, effective, and low-cost technique that can provide data for the atmospheric deposition of trace elements in even remote areas. Over the last few decades, among the different living organisms, mosses are the bioaccumulators that have been widely used for this purpose, as they display very unique characteristics, both morphologically and physiologically [6,14,15].

Mosses were first used as biomonitor s of the atmospheric fallout in the Scandinavian countries [16–19]. They have no rooting system; all the necessary elements and water are obtained directly through wet and dry deposition, while some trace amounts of nutrients may also come from the soil [11,20–25]. They grow up slowly and they can provide information about the atmospheric fallout over a long time of exposure. Each annual accumulation of trace elements can be distinguished with the use of the annual growth segments of mosses [26]. Mosses are suitable for monitoring elemental concentrations on a large geographic scale [6,8,23,27,28] while also achieving high-sampling-density networks [3,15,29].

The moss biomonitoring technique is used as part of a European monitoring program for air pollutants that has been performed since the 1990s on a regular basis (every five years) [30]. The “European moss survey” is performed under the auspices of the ICP Vegetation (International Cooperative Program on Effects of Air Pollution on Natural Vegetation and Crops), aiming at the atmospheric deposition of trace elements on mosses across Europe [13,31]. Greece contributed for the first time to such an extent to the European moss survey by providing data on the elemental concentrations in moss samples collected in all the northern part of the country.

Different statistical tools are usually applied in moss studies for the identification of the emission sources of the trace elements, such as the factor analysis (FA) and principle component analysis (PCA) methods [15,32]. In the present study, a more robust source apportionment technique, positive matrix factorization (PMF), was applied for the first time in mosses in the Greek territory. PMF displays enhanced features with respect to the FA and PCA methods, namely the use of the experimental uncertainty in order to weigh the data values and non-negativity constraints for the obtained factors [33]. It is one of the most popular source apportionment techniques for atmospheric aerosol and is extensively used in the framework of air quality management [34–36]. PMF is a receptor modeling tool that attributes the observed elemental concentrations to their major emission sources without “a priori” information on source chemical profiles [36–38]. To our knowledge, this source apportionment technique has been applied for the identification of natural and anthropogenic sources of trace elements in mosses in only very few recent research works [39,40].

The overall objective of this research was to study the bioaccumulation of trace elements in mosses of Northern Greece, to identify their sources by applying the positive matrix factorization model, and to establish a Greek database for future studies.

2. Materials and Methods

2.1. Study Area and Sampling

The “Moss survey” sampling protocol followed the instructions of the ICP Vegetation Monitoring manual; thus, only samples of natural growing pleurocarp mosses were collected. In drier areas—as Greece is—the taxa Hypnum cupressiforme Hedw., Pseudoscleropodium purum (Hedw.) M. Fleisch, Camptothecium lutescens (Hedw.) Schimp., and Homalothecium sericeum (Hedw.) Schimp. were among the recommended taxa to be collected [23,30,31]. All samples of fresh moss material were collected from open areas, at least 300 m from main roads and 200 m from populated areas, and from different substrate types (rocks, surface soil, branches, and near roots). It was recommended to make one composite sample consisting of five sub-samples from each sampling point, if possible, and to collect them within an area of about 50 × 50 m. Sub-samples were placed side by side in large plastic bags, which were tightly closed to prevent contamination during transportation.
For each sample, the amount of fresh moss collected for elemental analysis was about one liter (ICP Vegetation Protocol) [32].

The moss sampling took place in the area of Northern Greece during the end of the summer of 2016. There was no rain during the sample collection and no contact with surface water. Any extraneous materials that might have been found on the moss surface were removed manually from the samples. Mosses were not washed, and after sampling, they were frozen until further treatment according to the ICP Vegetation Protocol [31].

In total, 105 moss samples were collected, with the sampling sites’ altitudes ranging between 30 and 1450 m above sea level. More specifically, 95 moss samples were collected from 39.97° North to 41.65° North and from 20.97° East to 26.26° East, in a grid of 30 x 30 km (Figure 1), while the remaining 10 moss samples were collected from the area of Skouries (40°28′ N, 23°41′ E), close to active mining facilities. The area of Skouries is located almost in the middle of Northern Greece, in the Northeastern Chalkidiki peninsula (Central Macedonia Region, Chalkidiki Prefecture), and has had a long mining history since ancient times (6th century B.C.). In recent years, many studies have been performed on the environmental pollution of the area due to the mining activities [41–46]. The present study is the first one to use moss samples as monitors of trace elements originating from the mining activities in the Skouries area.

Among the moss taxa recommended for collection, in Northern Greece, the most commonly found taxon was the Hyphnum cupressiforme Hedw., and it was collected in the majority of the sampling sites (in 92 sites), with the other moss samples being Pseudoscleropodium purum (Hedw.) M. Fleisch, Camptothecium lutescens (Hedw.) Schimp., and Scleropodium tourretii (Brid.) L.F. Koch. From the Skouries area, the ten moss samples collected belonged to taxa found in great abundance in the specific area: Hyphnum cupressiforme Hedw., Homalothecium sericeum (Hedw.) Schimp., Isothecium alopecuroides (Lam. ex Dubois) Isov., Antitrichia curtipendula (Hedw.) Brid., Pterogonium gracile (Hedw.) Sm., and Dicranum scoparium Hedw. [47].

It must be noted that, according to the ICP Vegetation Protocol, when bryophyte species other than the main preferred ones (i.e., Hylocomium splendens (Hedw.) Schimp. or Pleurozium schreberi (Willd. ex Brid.) Mitt., which are species more commonly found in the northern European countries but are not so common in drier areas) are used for a survey, a comparison and calibration of their uptake of heavy metals relative to the main preferred species must be performed [31].

Figure 1. The moss sampling sites in Northern Greece.

2.2. Sample Preparation and NAA Analysis

After sampling, mosses were prepared and analyzed through neutron activation analysis (NAA) at the IBR-2 reactor of the Frank Laboratory of Neutron Physics, Joint Institute for Nuclear Research (JINR), in Dubna, Russia.

More specifically, samples were air-dried to a constant weight for 3 h at 40 °C, and they were then homogenized and pelletized using a press form. Each sample was packed
into plastic bags for short-term irradiation, and then into aluminum foil cups for long-term irradiation. Through a pneumatic system, REGATA, the packed samples were irradiated in two different irradiation channels of the IBR-2 reactor for short- and long-term irradiation. For the determination of the short-lived isotopes (Al, Na, Mg, Ti, Cl, Mn, V, Ag, Ni), samples were irradiated for 180 s, while for the long-lived isotopes (Ca, K, Sc, Br, Rb, Sr, Cr, Fe, Co, Zn, Th, U, As, Ce, Cs, Mo, Zr, Sb, Ba, La, Sm, Gd, Tb, Hf, Au), they were irradiated for 4–5 days. In accordance with the quality assurance procedures of the Moss Monitoring Manual of the ICP Vegetation Protocol [8,31], simultaneously with the moss samples, certified reference materials (NIST SRM 1547—peach leaves, NIST SRM 1575a—pine needles, NIST SRM 1633b—coal fly ash, NIST SRM 1632c—coal (bituminous), NIST SRM 2709—San Joaquin soil, and IRMM SRM-667—estuarine sediment), which were provided by the National Institute of Standards and Technology (NIST) and the Institute for Reference Materials and Measurements (ERM), were also irradiated in the same channels of the reactor and under the same conditions. The standard reference materials (SRMs) varied between 1% and 14%, with the exception of Mn, Ti, Mg, Br, and Hf, for which the relative differences were 20%. There was no use of correction factors in calculating the final elemental content for the moss species approved by the program, and no additional variability was added to the data.

After irradiation, samples were measured by High Purity Germanium (HPGe) detectors of 40% relative efficiency and 1.74 keV FWHM (full-width at half-maximum) at the 1332 keV line of $^{60}$Co. More specifically, for the determination of the short-lived isotopes, the samples that were irradiated for a short time period were measured with gamma spectrometry for 15 min immediately after their irradiation. Concerning the long-lived isotopes, samples were measured with gamma spectrometry once for 5 h after 3 days of their irradiation, and once more for 20 h at 20 days after their irradiation. The GENIE-2000 software was used for the analysis of the gamma spectrum. Based on the certified values of the reference materials and by using special software that was developed in the JINR [48], the concentrations of 34 elements in mosses were defined.

### 2.3. Positive Matrix Factorization (PMF) Analysis

The measured elemental concentrations were used for the application of receptor modeling for the identification of the sources of trace elements. More specifically, the positive matrix factorization (PMF) source apportionment method was applied by means of the EPA PMF 5.0 model [37].

The PMF model is a mathematical model based on the mass conservation between an emission source and a study site [49]. It apportions the concentration of each chemical element in each sample to the different sources impacting this element using the following mass balance equation

$$ c_{ij} = \sum_{k=1}^{p} g_{ik} \times f_{kj} + e_{ij} \quad (1) $$

where

- $c_{ij}$ is the concentration of a chemical element $j$ measured in sample $i$,
- $p$ is the number of factors (sources) that contribute to the measured concentrations,
- $g_{ik}$ is the contribution of the source $k$ to the sample $i$,
- $f_{kj}$ is the concentration of the chemical element $j$ in the source $k$, and
- $e_{ij}$ is the residual (the difference between the measured value and the value fitted by the model) for chemical element $j$ in sample $i$.

The model solves Equation (1) by minimizing the following object function:

$$ Q = \sum_{j=1}^{m} \sum_{i=1}^{n} \frac{e_{ij}^2}{s_{ij}^2} = \sum_{j=1}^{m} \sum_{i=1}^{n} \left( \frac{c_{ij} - \sum_{k=1}^{p} g_{ik} \times f_{kj}}{s_{ij}} \right)^2 \quad (2) $$

where $s_{ij}$ is the uncertainty of the measured concentration of chemical element $j$ in sample $i$, $n$ is the number of samples, and $m$ is the number of chemical elements [50].
Thus, as shown by Equation (2), the PMF solution is a weighted least squares fit, where the known standard deviations of the input concentration values ($s_{ij}$) are used for determining the weights of the residuals, $e_{ij}$. In addition, the model implements non-negative constraints [51,52]. The final output consists of two matrices: Matrix G, including the contributions of each source to each sample ($g_{ik}$), and Matrix F, including the concentration of each chemical element in each source ($f_{kj}$). This output depends on the number of factors/sources ($p$), which should be defined by the user.

The input database for the source apportionment analysis included 30 chemical elements (Na, Mg, Al, Si, Cl, K, Ca, Cd, Ti, V, Cr, Mn, Fe, Co, Ni, As, Br, Rb, Sr, Mo, Sc, Sb, Cs, Ba, La, Ce, Tb, Hf, Ta, and Th) that were detected in the 105 samples. The uncertainties of the concentrations of all chemical elements were calculated based on the sampling and analytical uncertainties. Elements with high uncertainty values (low signal-to-noise (S/N) ratio) were excluded from the analysis. In addition, four chemical elements (Mg, Al, Cd, and Th) were set as “weak” chemical elements because, based on the initial model runs, they produced high residual values. In the case of “weak” elements, the model triples all uncertainties associated with these chemical elements [53,54]. Additionally, an extra 10% modeling uncertainty was added in the model to account for modeling errors.

Solutions with different numbers of sources (ranging from 4 to 10) were examined [36]. Based on different criteria, such as the distributions of the residuals, the G-space plots, and the Q values, the best solution of the model was extracted, including five sources with a physical meaning. The final solution was based on 100 runs, while the rotational ambiguity of the solution was also assessed through the use of different $F_{peak}$ values (in the range $-1.0$ to $1.5$). The best solution was found for $F_{peak} = -0.5$.

3. Results
3.1. Elemental Concentrations in Mosses

The descriptive analyses (max, min, mean, median, and standard deviation) of the elemental concentrations of the moss samples collected from the whole region of Northern Greece are presented in Table 1, while the concentrations of mosses collected specifically from the area of Skouries are presented in Table 2. This distinction was performed in order to separately study the case of Skouries and to understand the impact that the mining activities have on the area. The results of the current study are in agreement with the data obtained from a previous moss biomonitoring study held in Northeastern Greece, close to the Bulgarian boarders [55]. A more detailed discussion of the measured elemental concentrations may be found in [56].

3.2. Source Apportionment of Elemental Concentrations

According to the PMF model results and all the performance criteria described above, the best solution that was extracted included the following five sources: soil dust, aged sea salt, road dust, lignite power plants, and a Mn-rich source. The chemical profiles of all the identified sources and the percentage of each chemical element assigned to each source are presented in Figure 2.

The soil dust source was identified by the high contribution of crustal elements, such as Mg, Al, Ti, Si, Ca, Th, Ba, La, K, and Fe [57]. More than 40% of the mass of key crustal elements (such as Si, Ca, K, and Mg) was assigned to this factor by the model. This source may represent the local soil dust resuspension or soil dust transported from greater distances, such as during the long-range transport of African dust [34]. It should be mentioned that the dry climate of Greece favors soil resuspension, even over long distances [58].
### Table 1. The elemental concentrations (in µg g⁻¹) in 95 moss samples collected in Northern Greece and determined by means of neutron activation analysis (NAA).

| Element | Na   | Mg   | Al   | Cl   | K    | Ca    | Sc    | Si    | Ti    | V    | Cr   | Mn   | Fe   | Cu   | Zn   | As   | Se   | Br   | Rb   | Sr   | Zr   | Mo   | Ag   | Sb   | Ba   | La   | Tb   | Hf   | Ta   | Th   | U    | Au   |
|---------|------|------|------|------|------|-------|-------|-------|-------|------|------|------|------|------|------|------|------|------|------|------|------|------|------|------|------|------|------|------|------|------|------|
| mean    | 1730 | 4432 | 7846 | 145  | 6360 | 8900  | 2.12  | 78458 | 440   | 10.08| 24.05| 2.45 | 11.07| 6.48 | 21.98| 52.13| 35.16| 0.28 | 0.06 | 0.27 | 0.06 | 104.7| 5.42 | 0.13 | 0.09 | 0.23 | 2.07 | 0.95 | 0.0123 |
| StDev   | 2266 | 2813 | 6812 | 68   | 2956 | 3236  | 1.93  | 64318 | 327   | 6.12 | 35.58| 200  | 5182 | 3.25 | 13.77| 50.14| 36.91| 0.25 | 0.02 | 0.39 | 0.06 | 12.4 | 5.40 | 0.12 | 0.09 | 0.23 | 2.44 | 0.60 | 0.0226 |
| median  | 196  | 705  | 1370 | 47   | 2180 | 3960  | 0.29  | 11500 | 97    | 2.61 | 11.50| 219  | 3770 | 1.69 | 7.26 | 37.60| 10.7 | 9.11 | 5.85 | 15.50| 38.20| 21.50| 0.23 | 0.05 | 0.69 | 1.01 | 151  | 5.53 | 0.13 | 0.82 | 0.14 | 1.76 | 0.40 | 0.0004 |
| min     | 30   | 30   | 30   | 30   | 30   | 30    | 30    | 30    | 30    | 30   | 30   | 30   | 30   | 30   | 30   | 30   | 30   | 30   | 30   | 30   | 30   | 30   | 30   | 30   | 30   | 30   | 30   | 30   | 30   | 30   | 30   | 30   |
| max     | 9230 | 46300| 46300| 380  | 17200| 23800 | 8.92  | 340000| 1760  | 35.40| 222  | 1090 | 20.70| 20.5 | 90.20| 56.30| 52.9 | 107.0| 239.0| 3.31 | 3.23 | 5.98 | 53.20| 35.2 | 0.57 | 4.72 | 1.08 | 13.6 | 3.36 | 0.0274 |

### Table 2. The concentrations of trace elements (in µg g⁻¹) in 10 moss samples collected only from the area of Skouries and determined by means of neutron activation analysis (NAA).

| Element | Na   | Mg   | Al   | Cl   | K    | Ca    | Sc    | Si    | Ti    | V    | Cr   | Mn   | Fe   | Cu   | Zn   | As   | Se   | Br   | Rb   | Sr   | Zr   | Mo   | Ag   | Sb   | Ba   | La   | Tb   | Hf   | Ta   | Th   | U    | Au   |
|---------|------|------|------|------|------|-------|-------|-------|-------|------|------|------|------|------|------|------|------|------|------|------|------|------|------|------|------|------|------|------|------|------|
| mean    | 1079 | 10,094| 11,795| 599  | 2078 | 10,090| 1.75 | 65,150| 652   | 11.4 | 11.14| 6.8  | 18.2 | 57   | 28.8 | 0.22 | 0.09 | 0.69 | 0.01 | 151  | 5.53 | 0.01 | 0.14 | 1.91 | 0.41 | 0.0097 |
| StDev   | 461  | 4353 | 3440 | 540  | 2827 | 2044  | 0.94 | 27,256| 608   | 3.12 | 3.46 | 2.4  | 3.30 | 12   | 7.6  | 0.05 | 0.05 | 0.12 | 0.04 | 87   | 1.85 | 0.04 | 0.06 | 0.30 | 0.10 | 0.0085 |
| median  | 901  | 11,350| 12,050| 353  | 6195 | 9270  | 1.48 | 56,050| 606   | 4.77 | 4.77 | 6.4  | 7.7  | 47   | 10.7 | 0.28 | 0.09 | 0.65 | 0.01 | 123  | 5.19 | 0.13 | 0.02 | 1.76 | 0.40 | 0.0089 |
| min     | 665  | 5850 | 7270 | 571  | 4910 | 4090  | 1.74 | 40,800| 352   | 4.52 | 65   | 20   | 52   | 15   | 13.9 | 3.05 | 0.05 | 0.06 | 0.13 | 0.08 | 73   | 3.45 | 0.08 | 0.08 | 1.27 | 0.36 | 0.0045 |
| max     | 1730 | 16,400| 17,300| 2070 | 14,800| 16,800 | 4.12 | 168,000| 1230  | 15.4 | 17.50| 10.6 | 138  | 72   | 15.4 | 17.50| 59   | 34   | 104  | 50.70| 0.33 | 0.14 | 1.03 | 1.28 | 367  | 8.79 | 0.18 | 1.71 | 0.27 | 2.52 | 0.67 | 0.0319 |
Figure 2. The chemical profiles of the soil dust, aged sea salt, road dust, lignite power plant, and Mn-rich source. The light blue bars (left axis) represent the concentrations as mass fractions, while the red dots (right axis) represent the percentage of each chemical element's mass that is assigned to each source.

The aged sea salt source was identified by the very high contribution of Na. Chlorine was also present in this factor, but in much lower concentrations than expected for the sea salt based on stoichiometry. The Cl/Na ratio for fresh sea salt is equal to 1.8 [59], while the respective ratio in this factor was below 0.01. This indicates the depletion of Cl from this source, suggesting that the sea salt particles deposited on mosses were not fresh and had previously interacted with anthropogenic pollutants [53]. A significant part of the Hf and
Ta mass (above 50%) was also apportioned to this factor. These two elements have been associated with heavy oil combustion [60] and may be indicative of shipping emissions arriving together with sea salt particles.

The dispersed road dust source included high loadings of Sb and As. This factor is related to vehicular traffic and reflects the road dust that has entered into the atmosphere through the wind action or through the turbulent action of motor vehicles passing across road surfaces [61]. More than 70% of the mass of Sb was assigned to this factor. Sb is a common traffic tracer, and is mainly associated with the brake pads in cars [22,37,62–65]. The dispersed road dust source also included high concentrations of crustal elements from the dust deposited in the road and resuspended due to vehicular traffic (such as Fe, Si, and Al), as well as Ba, an element that is also related to brake abrasion [65].

The lignite power plant source was identified by the presence of Ni, Cr, and Co. More than 60% of the Ni and Cr mass was assigned to this source. Ni is a common component of fly ash, while Cr and Co are linked to fossil fuel burning [37,66]. This factor is also influenced by high loadings of the V and Mg, which are also elements included in the fly ash produced by the burning process. A part of the fly ash may escape from the filters of the power plants and be emitted into the air. It should be noted that the contribution of this source is very high in the Skouries area and in West Macedonia, an area greatly impacted by the Ptolemaida lignite power plants. Regarding the area of Skouries, this source may be also related to local rocks, specifically amphibolites, which are considered to have derived from ophiolites, which are rich in Cr, Ni, and Co [67–69].

The Mn-rich source was characterized by high concentrations of Mn and was associated with mining activities. It should be noted that this source was more prevalent in the Skouries samples, further supporting its association with the mining activities in the area. Mixed sulphide and manganese deposits exist in the area north of Skouries, contributing to the observed Mn concentration [69].

The relative source contributions for each sample are presented in Figure 3. The average source contributions for the whole region of Northern Greece are presented in Figure 4. Among the five sources identified by source apportionment, the soil dust source was the one that contributed the most to the elemental concentrations found in mosses (46%), followed by the aged sea salt source and the road dust source.

![Figure 3](image-url) Figure 3. The relative contributions of the sources to each sample.
4. Discussion

Mosses are ideal bioindicators of trace elements. Moss biomonitoring is an efficient, non-expensive, and widely used method for the determination of the atmospheric deposition of trace elements. In the present work, 105 moss samples were collected from the region of Northern Greece (10 from the area of Skouries, known for its mining activities, and 95 from the remaining part of Northern Greece). They were analyzed using the NAA, and the concentrations of 34 elements were determined. The elemental concentrations were further exploited for the determination of the trace elements’ sources through the application of the positive matrix factorization (PMF) model. It should be noted that this is the first time that the PMF model has been used in conjunction with the moss biomonitoring technique for the identification of trace elements’ sources in Greece. PMF has also been used for moss elemental concentration source apportionment in a few recent studies in Europe and Asia, with positive results with respect to source identification [39,40].

As seen in Tables 1 and 2, significant differences in the elemental concentrations in mosses of the area of Skouries and the rest of Northern Greece are observed. For example, the mean values of the elements (Fe, Al, Mg, Cl, K, Ca, Sc, Ti, V, Cr, Mn, Co, Ni, As, Br, Ag, Sb, Cs, Ba, La) are higher in the samples collected from the area of Skouries than the rest of Northern Greece. This is more pronounced for Mn and Ni, which were found to be 1.5 times higher in Skouries in comparison to the remaining samples, and for Au, which was 80% higher in Skouries. The above-mentioned elements may be associated with the extraction of gold and, generally, with the mining activities taking place in the Skouries area. The main reason for these observed elevated elemental concentrations in the moss samples of Skouries is the resuspension of the soil dust that is released during the mining activities. The dust, which contains different trace elements, can be easily transferred by air, be deposited in the surrounding area, and be absorbed by the biota [46].

Several other studies concerning the levels of trace elements in different matrices (water, seaweeds, fish, sediments, soil) have been conducted over the last decades in the area of Skouries. For instance, high concentrations of As, Zn, and Mn (320–4100 μg g⁻¹, 940–4100 μg g⁻¹, and 3840–26,000 μg g⁻¹, respectively) have been measured in sediment samples collected close to the coastal mining facilities (Ierissos Gulf) [70]. Furthermore, high concentrations of Cr and Ni have been also measured in surface sediment samples in the area near the load-out facility of the mining operations in Stratoni Bay, and they were considered as the result of the weathering action of the rivers that flow into the Gulf [71,72]. Additional studies that have included water samples from Ierissos Gulf and soil samples from the Stratoni area have shown exceedances of the World Health Organization (WHO)
limit values and of the global soil mean values, respectively, mainly for the elements As, Sb, Cr, Ni, Cd, Pb, Mn, and Fe [43,45,73–75].

According to the PMF model results, five sources were identified: soil dust, aged sea salt, road dust, lignite power plants, and a Mn-rich source. Overall, the results indicate that the majority of trace elements found in mosses are related with soil dust particles that have entered the atmosphere through resuspension and transport mechanisms and are subsequently deposited on mosses. Relatively high contributions (on average 26%) from a geogenic source were also found in moss samples collected in Norway [39]. It should be noted that the arid climate of Greece favors the resuspension of the soil and road dust particles; with the aid of the local winds, the particles can easily travel over even further distances, influencing the elemental concentrations in mosses [40]. Nevertheless, anthropogenic sources have been also identified, with the most prevailing source being road dust from vehicular traffic. Xiao et al. performed a similar study in alpine ecosystems in China and also identified vehicular traffic as a major source contribution to moss elemental concentrations (average contribution of 15%) [40]. Sea salt particles were found to contribute significantly to the elemental concentrations as well; the respective source chemical profile displayed a low Cl/Na ratio, pointing towards aged sea spray produced through chemical reactions of fresh sea salt particles with anthropogenic emissions. Cl depletion in atmospheric aerosol has been observed to occur when urban pollutants, such as nitric and sulfuric acid, interact with sea salt particles to form sodium salts [53].

Based on the relative source contributions for each sampling site, the soil dust source and the aged sea salt contributed more than 60% to the majority of the moss samples, while the vehicular-related dust source was present in almost all samples (Figure 3).

The application of the source apportionment methodology led to the identification of two areas with significant impact from anthropogenic activities: the area of Ptolemaida in the region of Western Macedonia (sites x-30–x-42) and the area of Skouries (sites b-01–b-10). These two areas are both linked with intense anthropogenic activities, whose impact can be visualized through the high loadings of key anthropogenic elements in mosses and, correspondingly, high contributions from specific anthropogenic sources, as discussed below.

In the area of Ptolemaida, where there is a complex of lignite power plants, the concentrations of Ni, V, Cr, and Co were found in high levels, and these are directly related with the mining and burning processes of the lignite [37]. The lignite power plant source was found to contribute significantly to moss samples collected from this area (12% in comparison to 4%, which was the overall mean contribution for all samples). The second area, which corresponds to the area of Skouries, is characterized by intense anthropogenic activities, whose impact can be visualized through the high loadings of key anthropogenic elements in mosses and, correspondingly, high contributions from specific anthropogenic sources, as discussed below.

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