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Air Pollution Research Based on Spider Web and Parallel Continuous Particulate Monitoring—A Comparison Study Coupled with Identification of Sources

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Abstract: Air pollution is monitored mainly in urban or industrial areas, even if it is known that in rural ones, low emission can significantly worsen air quality. Hence, cheap and easily accessible methods of monitoring are needed. Recently, spider webs biomonitoring is getting popular, however, there is no information about its comparison with active methods. In this study, PTEs accumulated on spider webs were compared with results from continuous particulate monitor (CPM). Generally, higher potentially toxic elements concentrations were noted in spider web, with exception in the case of Zn. Zn may be present rather in smaller fractions, hence it needs more time for accumulation on spider web while it is easily collected by CPM. Higher concentrations of other elements on spider webs may result from formation of aggregates which could not be reported in PM_{10} sampling (CPM). What is more, the order of the most and the least accumulated elements were similar and the percentage share of studied elements was coherent in most cases, proving that this new tool prospers to become commonly used in biomonitoring. Additionally, to identify possible sources of pollution air backward trajectories and trajectory frequencies for Kotórz were prepared based on the HYSPLIT model.

Keywords: biomonitoring; potentially toxic elements; spider web; PM; continuous particulate monitor

Citation: Stojanowska, A.; Mach, T.; Olszowski, T.; Bihałowicz, J.S.; Górka, M.; Rybak, J.; Rajfur, M.; Świsłowski, P. Air Pollution Research Based on Spider Web and Parallel Continuous Particulate Monitoring—A Comparison Study Coupled with Identification of Sources. *Minerals* **2021**, *11*, 812. https://doi.org/10.3390/min11080812

Academic Editors: Romain Millot, Jiubin Chen and David Widory

Received: 25 June 2021
Accepted: 23 July 2021
Published: 27 July 2021

1. Introduction

Particulate matter (PM) is a mixture of solid and liquid particles, suspended in the air, originating from both natural and anthropogenic sources [1,2]. In Europe, PM is considered one of the major air pollutants [3] and according to WHO, it is responsible for causing respiratory diseases often leading to premature deaths [4]. Considering the hazardous impact of PM, the monitoring of the particles in the air is essential issue nowadays, especially in urbanized areas, where people are exposed to higher PM levels, which are of great focus [5–7]. For instance, in Poland, the annual air quality assessment in terms of PM_{10} and $PM_{2.5}$ concentrations is carried out mainly in big cities or areas where industries suspected of emitting hazardous pollution are located. However, the air quality in the nearby, usually rural, areas, situated on the leeward side, are often not considered in the monitoring but might be contaminated as well.

Another thing is that usually, to obtain very accurate information about air quality, the specific instrumentation is used, i.e., active samplers. However, in some cases where their use is impossible due to financial issues or limitations in the study area, bioindicators can be applied. In bioindication, the assessment of environmental pollution can be conducted with the use of living organisms, like lichens [8], mosses [9,10], tree leaves [11] or their products, e.g., spider web [12]. The use of spider webs in biomonitoring is quite a new idea, but it has been already proved that this tool can give good results in the case of potentially toxic elements (PTEs) accumulation. Spiders build their webs in various places (both natural and polluted). With this feature, spider webs can be used regardless of air pollution and hence the way to obtain them is easy and cheap. There is also a possibility to determine the exact time of exposition by destroying the old web and observing the moment of new construction. Another idea is to use the clean web, obtained from laboratory-bred spiders, which facilitates the determination of exposure time. Additionally, the method is noninvasive and can be considered no waste. The possibility of the use of spider webs in assessing air quality has been performed before, and satisfying results were obtained [13–17]. The webs have already proved to be a good passive sampler in the case of potentially toxic elements [13,16,18,19] or polycyclic aromatic hydrocarbons (PAHs) [20,21].

The papers mentioned above prove that spider webs are nowadays a subject of interest for many scientists. The results from spider webs were once compared with lichens [15] and once with mosses [22] proving that the element mass fractions are significantly higher for spider web which might suggest that webs could be used in all cases where the results for lichens or mosses are under the detection limit. There was also one intent aiming at the comparison of two selected metals with different fractions of PM obtained by cascade impactors of Harvard type. However, the comparison of the usefulness of spider webs has never been checked regarding an active PM sampling by a continuous particulate monitor (CPM) equipped with metal concentration in PM_x online analyzer.

In the present study, the comparison of metal concentration obtained from spider web monitoring using atomic absorption flame spectrometry (F-AAS) with the results of PM_{10} elemental composition measured online using energy-dispersive X-ray fluorescence (EDXRF) was conducted. Then the relations between results from both methods were checked. Additionally, enrichment factor was calculated to indicate which element is the most problematic in the study area and then backward trajectories and trajectory frequencies were presented in order to verify from which areas the pollution could come from. The major goal was a verification and validation of results from the bioindicator (spider web) method with EDXRF data. The bioindicators are used widely but the question about quantity and quality of environmental answers is still open. Therefore, in this paper, the investigation on such comparison should yield new valuable and methodically confirmed universal data, interesting for other international readers.

2. Study Area

Kotórz Mały is a small village (approx. 1000 inhabitants) in the Opolskie Voivodship, southwestern Poland (Figure 1). According to the report from 2019 presented by Wojewódzki Inspektorat Ochrony Środowiska—Regionalny Wydział Monitoringu Środowiska (Province Inspectorate of Environmental Protection—Regional Department of Environmental Monitoring) [23] the concentrations of given elements (Pb, As, Cd, Ni) in PM_{10} (particulate matter with a diameter of 10 microns or less) did not exceed the limits in the area of Opolskie Voivodship. In terms of the concentration of PM_{10}, the measurements carried out in 2019 revealed that the annual average value remained below the permissible level. However, the daily average values were exceeded, considering the criteria defined for the protection of health (50 $\mu g/m^3$), at five measuring stations [23]. We suppose that in this area in winter the local pollution originating from house heating dominate, or long-range transport can have a significant role in here, bringing the pollution from outside the locality. According to Olszowski in Kotórz Mały we can distinguish two zones in terms of dominating heating system [24]. In the first zone, predominated by rural buildings, 91% of the households use coal for heating processes. The second one is the modern building zone, where the production of heat energy is based on fuel gas (73%). Therefore, we can distinguish local sources of pollution, originating from the area of the village, i.e., coal burning for home heating purposes but also railway tracks, polish industry pollution sources (Figure 1A–I), and cross-border sources of pollution.

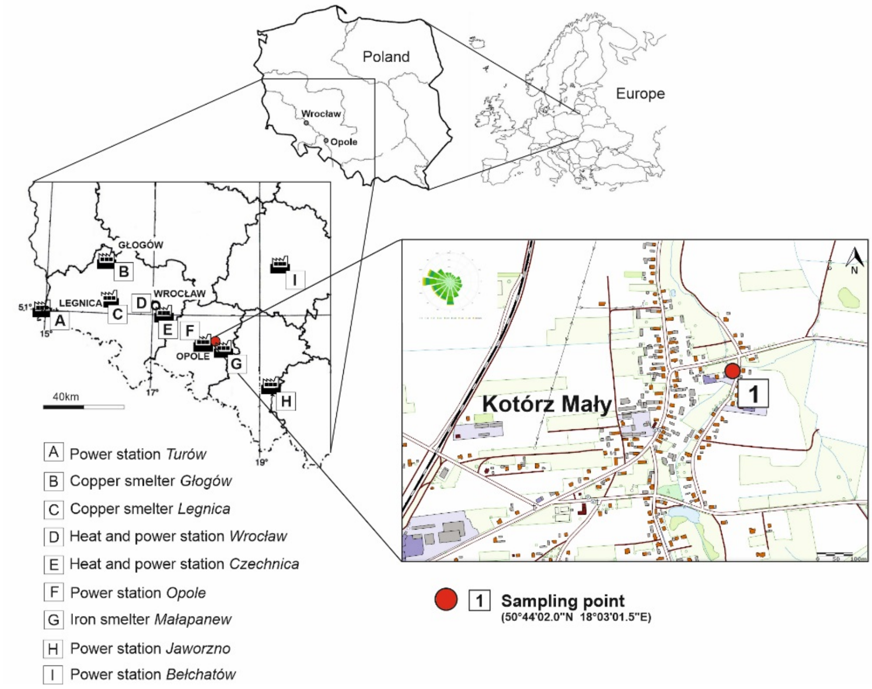

Figure 1. Location of the study area.

As presented on Figure 1, in the nearby voivodships many power stations are located i.e., Turów, Jaworzno, Bełchatów, and Opole. About 220 km west from Kotórz Mały lies Turów power plant which is known to be the second most polluting industry in Poland [25] and it is responsible for 40% of the dust pollution in the whole voivodship [26]. Other power stations are located in Jaworzno (100 km, southeast), Bełchatów (115 km, northeast), and Opole, only about 10 km southwest from Kotórz. What is more, heat and power stations in Wrocław (80 km, northeast) and Czechnica in Siechnice (70 km, northwest) are located nearby. As Opole and Jaworzno power stations and Wrocław and Czechnica heat and power stations are coal-fired, produced emissions are strictly connected with the process of coal burning. Coals from the Upper Silesian Coal Basin are known to contain Cr, Ni, Pb, and Zn [27], which by the combustion process are accumulated in the bottom and fly ash and then can be released to the atmosphere [28,29]. On the other hand, power stations Turów and Bełchatów are based on the lignite-burning for power production [30]. The amounts of potentially toxic elements in the ashes from lignite combustion in Poland are similar to the world-averages concentrations [31]. The ashes, produced in the process of lignite burning, contain following elements, presented in descending order Sr, Ba, Cr, Zn, Cu, Ni, As, Pb, Co [31]. Additionally, Cu smelters are situated in the area of Legnica and Głogów 140 and 170 km away from Kotórz Mały, respectively. In this region atmospheric aerosols can be characterized by the presence of Cu, Pb, Ni, Zn sulphides but also of metallurgical alloys varying in composition (Cu-Zn, Pb, Pb-Cu) [32]. Additionally, recent biomonitoring studies also provided the information about air contamination by Cu, Zn, and Pb in both of these regions [15,17]. In addition, an iron smelter—Małapanew in Ozimek can contribute to the air pollution by emitting the Fe particles to the atmosphere, however, from what is known for authors, now the activities in this area are much limited than in the past. Nowadays it deals mostly with the PM_{10} and $PM_{2.5}$ exceeding [33]. Apart from this, a few cross-border sources of pollution exist, located in the neighboring countries, i.e., Czech Republic (Ostravsko-karvinská Basin and North Bohemian Basin) or in Slovakia (Košice). In Košice region coke and steel production and iron metallurgy are placed. A confirmation of their negative impact on air pollution, especially on Fe emission, is the fact that high concentrations of studied elements (i.e., Fe, Mn, Cr, Pb, Zn) were found in the proximity of the ironworks [34]. In eastern part of Czech Republic steel manufacturing conurbation is located, which in known from emissions of high amounts of Fe, but also Zn, Cr, Pb and Mn in smaller quantity [35]. On the other hand, North Bohemian Basin is a part of Europe, known by the name of "black triangle", where high amounts of pollution are emitted [36]. This region is connected with electromechanical and metallurgical activities and brown coal mines and power plants are located there [36]. From this region following pollution may origin: e.g., Fe from industrial combustion of lignite, Pb connected with chemical works and lignite combustion and also Cu, due to the activity of a non-ferrous smelter in Príbram [37].

3. Meteorological/Environmental Parameters

The year 2019 was considered one of the warmest in comparison to previous years. In general, the annual average temperature in Poland amounted to 10.2 °C. In terms of precipitation, 2019 was classified as normal. Annual precipitation in Poland in this period amounted to 556 mm while in Opole to only 469.5 mm. During the samples collection, the average temperature in February amounted to 4 °C while in March about 6 °C [23]. The voivodship where Kotórz Mały is located the dominant winds blow from west and south [38] as also presented on the Figure 1.

4. Methods

4.1. Monitoring with Continuous Particulate Monitor

Samples Collection

CPM with EDXRF (PX-375 Horiba analyzer, HORIBA ltd., Kyoto, Japan) was used in this study to obtain the results concerning the elemental composition of PM_{10}. The PX-375 analyzer provides rapid air pollution measurements by conducting online automatic PM sampling characterized by excellent sensitivity and precise performance. The PM mass is measured continuously utilizing beta ray attenuation and then using nondestructive energy-dispersive X-ray fluorescence (EDXRF) spectroscopic analysis the quantitative and qualitative elemental composition can be obtained already in the field. Uncertainty of this method for given elements is as follows: ± 1.1 ng/m^3 for Mn, ± 153.2 ng/m^3 for Fe, ± 4 ng/m^3 for Cu, ± 12.4 ng/m^3 for Zn, ± 5.2 ng/m^3 for Pb, ± 50.7 ng/m^3 for Al.

In the process of PM collection, a two-layer nonwoven polytetrafluoroethylene (PTFE) fabric filter (HORIBA TFH-01 membrane), in the form of roll, was used as a filter tape. The manufacturer ensures collection rate up to 99.97%. Each roll has a length of 21 m and 40 mm width. The filters are characterized by thickness of 140 µm and the pore size in the filter was equal to 1 µm [39]. In general PTFE material is a fluoropolymer, characterized by an excellent chemical inertness and thermal stability, hydrophobicity, low surface energy and also low friction coefficient [40] after [41,42].

The air samples acquisition was characterized by the flow rate equal to 16.7 dm^3·min^{-1}. Every sixty minutes beta ray attenuation analysis was conducted to assess the exact mass quantity. This measurement is based on law which says that absorbed radiation is exponentially dependent only on the mass of filtered material [43]. According to that at first beta radiation was emitted at empty filter, then there was time for sample acquisition and the particles were adsorbed on the filter tape. Considering the difference between these two measurements the result, in the form of collected PM_{10}, was given. After that the filter tape is moved, the new measurement begins. The analysis was performed for 500 s, operated at 15 kV or 50 kV voltage (depending on the studied element). At the same time, continuously, a subsequent sample was collected.

A standard reference material SRM 2738 (air particulate on filter media), certified by NIST, was used to acquire a quality control for the machine and to define the elemental quantification of X-ray spectra. To calibrate the machine, the blank tape was checked three times and finally the mean value was taken. The calibration of the CPM was done two times by the qualified Horiba employees: at the beginning of the experiment and at the end, however, a few times during the sampling DryCal Defender 530 was used to make sure the flow did not change. The lowest detection limits (LDL) taken as a double the standard deviation of the analyzed blank samples were as follows: Al (56.7 ng/m^3), Cu (1.85 ng/m^3), Fe (7.00 ng/m^3), Mn (1.45 ng/m^3), Pb (1.05 ng/m^3), and Zn (1.25 ng/m^3). The repeatability of the obtained results was within ±2% of the equivalent film value. Additionally, in the information provided by the producer, it was shown that a strong correlation exists between the metal results given by CPM EDXRF (Horiba, PX-375, HORIBA Ltd., Kyoto, Japan) and conventional wet mineralization and measurement using ICP-MS.

CPM was placed in Kotórz Mały (Figure 1) and during about one month (7 February–17 March 2020), the hourly measurements were carried out continuously. Then the daily average values for this period were calculated.

4.2. Air-Mass Back Trajectory Analysis

To identify the possible sources of pollution, connected with long-range transport, movements of air masses concerning 24-h backward trajectories for Kotórz were constructed based on NOAA HYSPLIT model [44,45]. In addition, the meteorological data were acquired by the access to Gridded Meteorological Data Archives from National Oceanic and Atmospheric Administration (NOAA; www.ready.noaa.gov, accessed on 21 July 2021). Back trajectories of air masses were calculated for chosen days of spider web sampling period (7 February–17 March 2020) where higher than normal episodes of PM_{10} and selected metal concentrations were found (Figure 2). For each selected day, four 6-hourly trajectories at 500, 1000, and 1500 m.a.s.l. were calculated taking into account the following ending times: 00:00, 06:00, 12:00, and 18:00 UTC + 1 h.

Additionally, for long-term analysis, the maps of trajectory frequencies were constructed. Different colors indicate different frequencies [%] of the air mass movement crossing over a given geographical sampling point.

4.3. Enrichment Factor

Since the Horiba PX-375 was also analyzing the concentration of the aluminum in the ambient air, we were able to calculate the enrichment factor EF of elements collected in the air samples. The EF is defined [46]:

$$EF = \frac{\frac{C_{x,m}}{C_{Al,m}}}{\frac{C_x}{C_{Al}}} \quad (1)$$

where $C_{x,m}$ and $C_{Al,m}$ are concentrations of element x and aluminum in PM_{10} measured in our experiment while C_x and C_{Al} are concentrations in the upper crust according to [47]. According to [48] the EF values can be divided into 5 classes representing the level of enrichment (Table 1).

Table 1. EF classes according to [48].

EF Value	Level of Enrichment
$EF \leq 2$	minimal
$EF \in [2,5]$	moderate
$EF \in [5,20]$	significant
$EF \in [20,40]$	very high
$EF > 40$	extremely high

4.4. The Concentrations of Metals in PM_{10}

The PX-375 was analyzing concentrations of selected metals x in PM_{10} fraction in the atmospheric air $C_{x,V,i}$ in $\frac{ng}{m^3}$, the concentration of PM_{10} $C_{PM_{10},V,i}$ and total mass of the sample $M_{PM_{10},i}$ in 1 h intervals numbered by index i. The spider webs were collecting metals constantly, in the same total period as PX-375 so we had to find the total mass of PM_{10} collected during the whole experiment and masses of metals. The mass of PM_{10} collected in the whole experiment was simply the sum of masses of all n samples.

$$M_{PM_{10}} = \sum_{i=1}^{n} M_{PM_{10},i} \tag{2}$$

The calculation of the masses of metals is more tricky since as a result, we obtain the volumetric concentration $C_{x,V,i}$, firstly the volume of the analyzed air in sample number i have to be found:

$$V_i = \frac{M_{PM_{10},i}}{C_{PM_{10},V,i}} \tag{3}$$

And then the mass of the metal x in sample i can be expressed as:

$$M_{x,i} = C_{x,V,i} \cdot V_i \tag{4}$$

It leads to the formula for the mass of the metal in the whole experiment:

$$M_x = \sum_{i=1}^{n} \frac{C_{x,V,i}}{C_{PM_{10},V,i}} M_{PM_{10},i} \tag{5}$$

Therefore, we were able to calculate the content of these metals per mass of PM_{10}.

$$C_{x,m} = \frac{M_x}{M_{PM_{10}}} \tag{6}$$

We recalculated these values to determine the content of the selected metals in mg of the metal per kg of particulate matter. The mass concentration of metal x denoted as $C_{x,m}$ was determined as the ratio of atmospheric air volumetric concentration $C_{x,V}$ and concentration of PM_{10} $C_{PM_{10},V}$:

$$C_{x,m} = \frac{C_{x,V}}{C_{PM_{10},V}} \tag{7}$$

4.5. Biomonitoring with Spider Webs

Sampling Collection and Characteristic

Two species from the family Agelenidae, *Tegenaria agrestis* (WALCKENAER, 1802) and *Eratigena atrica* (C.L. KOCH, 1843), have been chosen for studies. In previous studies [20], we found that agelenids are the best choice for biomonitoring as they weave large and dense webs known as funnel webs which are not sticky and stretch out horizontally like a carpet with tubular retreat inside of spiders. In general, spider web is a silk material, which is made up from protein named spidroin (spider fibroin). Spidroin is built of 100–400 amino acids (mostly glycine 30.2% and alanine 24.3%). Glycine is responsible for elasticity of the web while alanine gives it the strength. Other amino acids building the web are as follows: serine, proline, glutamine, leucine, valine, tyrosine and arginine. The exact composition of these proteins is dependent on e.g., species and diet [49]. The deposition of heavy metals on webs has been studied in following researches [19,50]. Hose et al. [50] showed that heavy metals (Pb, Zn) are deposited mainly on web surfaces in cribellate spiders (*Badumna socialis* and *Stiphidion facetum*). The authors proved that washing webs with diluted acid reduced metal concentrations up to 80%. Cribellate webs are not sticky and trap prey and particulates in the dense network of silk fibers. The way of trapping air contaminants by spider webs of another family of spiders (Agelenidae) has been studied by Rybak et al. [19]. The webs of Agelenidae are also not sticky. The authors compared unwashed webs with washed once (shampoo and organic solvent acetone from MERCK) and noted a significant decrease in the of heavy metals' concentration (nearly up to 70%) which also suggests that heavy metals are mainly deposited with dust particles on the web surface [19]. However, in both studies, some parts of studied metals were not removed by the washing which could be attributed to internal contamination or other types of deposition mechanisms might be possible.

The newly woven webs (after the removal of an old web) were often visited and observed in the place of study, and therefore, after a defined exposure time for the creation of the new construction, they were removed and preserved for further analyses. These in situ samples of spider webs were collected from secluded locations which provided them the protection from unfavorable weather conditions. Additionally, we used webs derived from laboratory breeding of spiders. The already woven webs (from breeding containers) were deployed on plastic Petri dishes and closed in order to protect them from pre-exposure pollution. Spider webs of similar age, size and weight were used in this study. Then the dishes with spider webs were fixed at sampling sites with hot glue. The 10 prepared samples were placed in the close proximity to Horiba apparatus, on about 1.5 m height. After the exposition to pollutants for a defined period of time (approx. one month: 7 February–17 March 2020), the samples were collected with the use of glass, sterile baguettes and placed in sterile glass vials until further analyses (methodology according to [14,16,20,50]. Firstly, the webs were cleaned to remove accidental artefacts. Then they were conditioned for 24 h at the temperature of 20 ± 2 °C and 40 ± 5% humidity and next they were weighted three times using analytical balance Radwag AS 60/C/2 (minimum weight 1 mg, readability 0.01 mg, repeatability 0.04 mg). The samples were weight at a temperature of 23 ± 2 °C and relative humidity of 40 ± 5%). The average weight of the spider web sample was equal to 9 mg. The preexposure control webs, obtained from laboratory breeding, were previously analyzed in terms of chosen element concentration and revealed negligible values. According to the fact that most of the webs were collected from laboratory breeding spiders, we suppose that the concentration of selected by us elements on clean webs (before exposition) was negligible.

4.6. Metal Concentration Analyses

The mineralization and analyses of mineralized spider web samples were performed at the Institute of Environmental Engineering and Biotechnology, University of Opole (Opole, Poland).

Concentrations of Mn, Fe, Ni, Cu, Zn, Cd and Pb were determined in spider webs. After exposure, the research material was transported to the laboratory, homogenized, and digested in Teflon vessels. The webs were mineralized in a mixture of 5 cm^3 of nitric acid HNO_3 (65%, Merck) and 3 cm^3 of H_2O_2 (30%, Merck) at 180 °C for 20 min using a Speedwave Four closed microwave system from BERGHOF, DE. This process was carried out at 220 °C for 20 min and was performed twice to ensure complete digestion of all dust samples according to [51].

Samples were transferred quantitatively, after mineralization, into a 25 cm^3 (class A) volumetric flask with deionized water. Metals were determined using an atomic absorption flame spectrometer (F-AAS) type iCE 3500 (series 3000) made by Thermo Scientific, USA. The F-AAS method was used previously in analyses of potentially toxic elements collected on spider web and satisfying results were obtained [15].

4.7. Quality Assurance and Control

In Table 2, the instrumental detection limits (*IDL*) and instrumental quantification limits (*IQL*) for the spectrometer iCE 3500 are presented [52,53].

The values of the highest concentrations of the models used for calibration (2.0 mg/dm^3 for Cd, 5 mg/dm^3 for Ni, Cu, Zn, Pb, 7.5 mg/dm^3 for Mn and 10 mg/dm^3 for Fe) were approved as linear limits to signal dependence on concentration. Calibration of the spectrometer was performed with an internal standard solution from ANALYTIKA Ltd. (CZ). Additionally, in Table S3, concentrations of heavy metals in certified reference materials BCR-482 lichen, produced at the Institute for Reference Materials and Measurements, Belgium, were shown.

Table 2. The instrumental detection limits (*IDL*) and instrumental quantification limits (*IQL*) for the spectrometer iCE 3500 (mg/dm^3) [52,53].

Metal	*IDL* (mg/dm^3)	*IQL* (mg/dm^3)
Mn	0.0016	0.020
Fe	0.0043	0.050
Ni	0.0043	0.050
Cu	0.0045	0.033
Zn	0.0033	0.010
Cd	0.0028	0.013
Pb	0.0130	0.070

5. Results

5.1. Spider Webs Monitoring

The monitoring with the use of spider webs revealed various concentrations of seven selected PTEs (Fe, Pb, Zn, Cu, Mn, Cd, and Ni; Table S2). The concentrations of Cd and Ni in the spider web were below the detection limit, hence their exact determination was impossible and they were omitted in the later part of the paper. The most abundant element on the spider web was Fe, which concentrations varied greatly with min. 1805 mg/kg and max. 2.4191 mg/kg. The next one was Pb and its concentrations were about one order of magnitude smaller than for Fe. In the case of Pb, the results differed from 173 to 2245 mg/kg. Two times smaller results were obtained for Mn, ranging from 168 to 1418 mg/kg. As the least abundant turned out to be Zn (min. 212 mg/kg, max. 687 mg/kg) and Cu (min. 60 mg/kg, max. 136 mg/kg).

5.2. Continuous Particulate Monitor

To confront the information obtained by spider webs monitoring CPM was used. Air quality monitoring with the use of CPM provided hourly results of PM_{10} concentrations which were then averaged. The minimal value of daily average amounted to 10.47 µg/m^3 while the maximum was 36.8 µg/m^3. In the sampling period, the exceeding of the maximum daily level for PM_{10} (i.e., 50 µg/m^3) was not observed during the whole period, and the average value of PM_{10} collected by CPM during sampling amounted to 20.53 µg/m^3. However, in the collected PM_{10} the presence of potentially toxic elements such as: Fe, Mn, Cu, Zn and Pb were noted.

5.3. Enrichment of Samples

The assessment of the enrichment in the studied elements was considered to be very important as the study site was located in the inhabited area. The enrichment factor (EF) shows a value enabling the quantitative determination of the anthropogenic influence on element concentration in PM. We calculated this factor for the samples collected by Horiba PX-375 and aluminum was used as the reference element. The reference concentrations in the upper crust were taken from [47]. The results are presented in Table 3. According to Table 1, the results for Zn and Pb indicated extremely high enrichment while EF for Cu is very high. In the case of Fe, there is only minimal enrichment whereas Mn shows moderate enrichment.

Table 3. EF for the elements in PM_{10}.

Element	Cu	Zn	Pb	Mn	Fe
EF	30.4	192	225	2.33	0.853

5.4. Backward Trajectories and Trajectory Frequencies

After indication of the possible problematic elements it was crucial to determine their origin. The concentrations of PM_{10}, Zn, Pb, and Fe were presented in Figure 2 and daily variation of these concentrations was observed depending on the specific day of the measurements. Such differentiation can occur when local air quality is influenced by regional or long-range transport. However, during a few days noted concentrations were much higher than in others. According to the most distinctive peaks, as can be seen in Figure 2, six episodes (A—08.02, B—17.02, C—28.02, D—04.03, E—09.03, F—16.03) were distinguished. Then, for each of these days, the maps of backward trajectories were constructed and presented in Figure 2. Creating these graphs can help us to indicate the potential source of pollution during each selected day.

In Episode A, noted concentration of Fe was the highest in the whole sampling period and it was shown that Fe was the predominant air pollutant during this day. According to air mass backward trajectories, this high Fe concentration might be enhanced by the transport of air mass from the Małapanew iron smelter, the activity of which, related to steel casting, classified the plant as very harmful to the environment in previous years [54]. Nowadays, however, the plant is known to work to a much lesser extent but possibly it is still emitting pollution. Another thing is that part of the winds pass through Hungary and could also bring the pollution from over there. According to [55] and the studies conducted in the area of Budapest in the total measured trace element concentrations, Fe was the most abundant (accounted for about 87%) and was followed by Zn, Pb, Cu and Mn. Additionally, in general, the Fe presence can be also ascribed to rail-wheel-brake interactions [56] as the railway tracks are located nearby.

High concentrations of PM, Fe, and Zn were noted in Scenario B and the air mass back trajectories indicated that the pollution could be possibly brought from the parts of Hungary, transporting the elements as listed above in Scenario A. However, according to the fact that the pollution during this day was relatively not high when compared to other episodes, hence, possibly the pollution may rather originate from local pollutants like railway tracks (Fe) or car traffic (Zn).

Episode C was characterized by quite high concentrations of Zn, Pb, and PM. Considering the prevailing wind directions during this day, we can assume that the pollution comes from the power station Turów (from west), which is lignite-fired and known to contribute to pollution with Zn, Cu, and Pb [31]. The observed winds can also cross by Wrocław heat and power station and Opole power station, which are coal-fired, leading to production of Pb and Zn. What is more, Zn as well as Pb, generated in the coal combustion processes, mostly accumulate in the fly ashes [29,57] which enhance their transport. Hence, it is understandable that in the case of Episode C, where the winds coming through this regions, relatively high values of Zn and Pb can be observed. Moreover, the high peak of PM_{10} could be also connected with the transport of pollution from further regions (i.e., Ústí nad Labem region, north-western Czech Republic) from where particles of Fe, Pb but also Cu can be transported [37].

In Episode D, high concentrations of PM_{10}, Fe, Zn and Pb were found. As we can notice, the structure of the highest points in this episode is a little more complicated—at first, high Fe and Zn concentrations are observed, while PM maximum point during this episode is the next day just right after the maximum of Fe and Zn. The day in which high Fe and Zn concentrations are found with relatively not high PM concentrations may indicate the observation of Fe and Zn rich air mass inflow. Having a look at the map of air masses backward trajectories, it can be seen that at first air masses could be brought from the area of the eastern Czech Republic where steel manufacturing conurbation of Ostrava is located, which is known for episodes of high pollutant concentrations [58]. In this region, the problem of contaminated air pollution results from different sources, such as steel and coke plants, low emission, coming from the burning of waste or coal powder, and traffic [59]. It was also shown that raw iron production contributes to about 30% of the coarse aerosol mass during the post-smog period [59]. In another study, the pollution produced in this area was recognized to contain high amounts of Fe (stating about 75–87% of the total sum of monitored potentially toxic elements). Other important elements were as follows: Zn (7.1–11%), Cr (2.3–6.8%), Pb (0.3–5.8%), and Mn (1.4–2.4%) [35]. This information confirms the hypothesis that elevated PTEs amounts can result from transboundary pollution. However, similarly to Scenario C, high concentration of Pb simultaneously with high concentration of Zn can be also an indication of the pollution brought from Turów and Opole power stations, coming from the west direction. Even though, it is supposed to be in smaller quantities, according to the fact that in the second day of this episode dominating wind direction change (south to west), a decrease of Fe, and, Pb concentration can be noted.

High PM and high Fe concentrations were found in the case of Episode E. Moreover, a peak in the case of Zn concentration was observed and a small peak of Pb. In this case, air masses could be brought mainly from the area of north western Czech Republic but also from the region of Ostrava. Both of these regions can be suspected of Fe, Pb and Zn pollution [35,37]. Some of the trajectories pass also through the region of polish Cu-smelters (Legnica and Głogów), from which transport of PM bearing Cu, Zn, Pb can be suspected [32]. In this episode, as well as C and D, the possibility of transport of pollution from Turów occurs, where lignite-fired power station is located. Hence, emitted pollution are supposed to be strictly connected with the process of lignite burning, which is proved to introduce Pb and Zn to the atmosphere [31].

Episode F presents high Fe concentrations and slightly lower PM when compared to other episodes. Considering that, we suppose that similarly to Episode A, collected sample must correspond to air masses enriched in Fe particles. In this case, the map of air masses backward trajectories indicates on emission originating from an industrial complex (composed of coke and steel production and iron metallurgy), located in the area of Košice (Slovakia). This region is known to be the dominant industrial source of air pollution, characterized by exceeding of daily limits for PM_{10} [60]. Additionally, according to [34] the maximum concentrations of all studied elements (especially Fe) were recorded at sites localized in the proximity of the ironworks, indicating its impact on air quality. Hence, it is supposed that in the case of favorable direction of wind, as in Episode F, the pollution could be also brought from there to Poland. Additionally, some of the winds reach the Hungary. Hence, it is supposed that pollution like Fe accounting for almost 90% of the total measured trace element concentrations [55] but also Zn, Pb, Cu, and Mn could be transported from over there.

What is more, the map of trajectory frequencies for this period presents that most of the occurring winds come from the S/SW/SE parts, which is in accordance with the general dominant wind directions in this region [38] also presented as wind rose in Figure 1. This could enhance not only the transport of air masses from polish industry sources located in the proximity of Kotórz Mały but also from the cross-border sources of pollution. These wind directions are the main factor determining elemental composition of pollution on spider web during this sampling period.

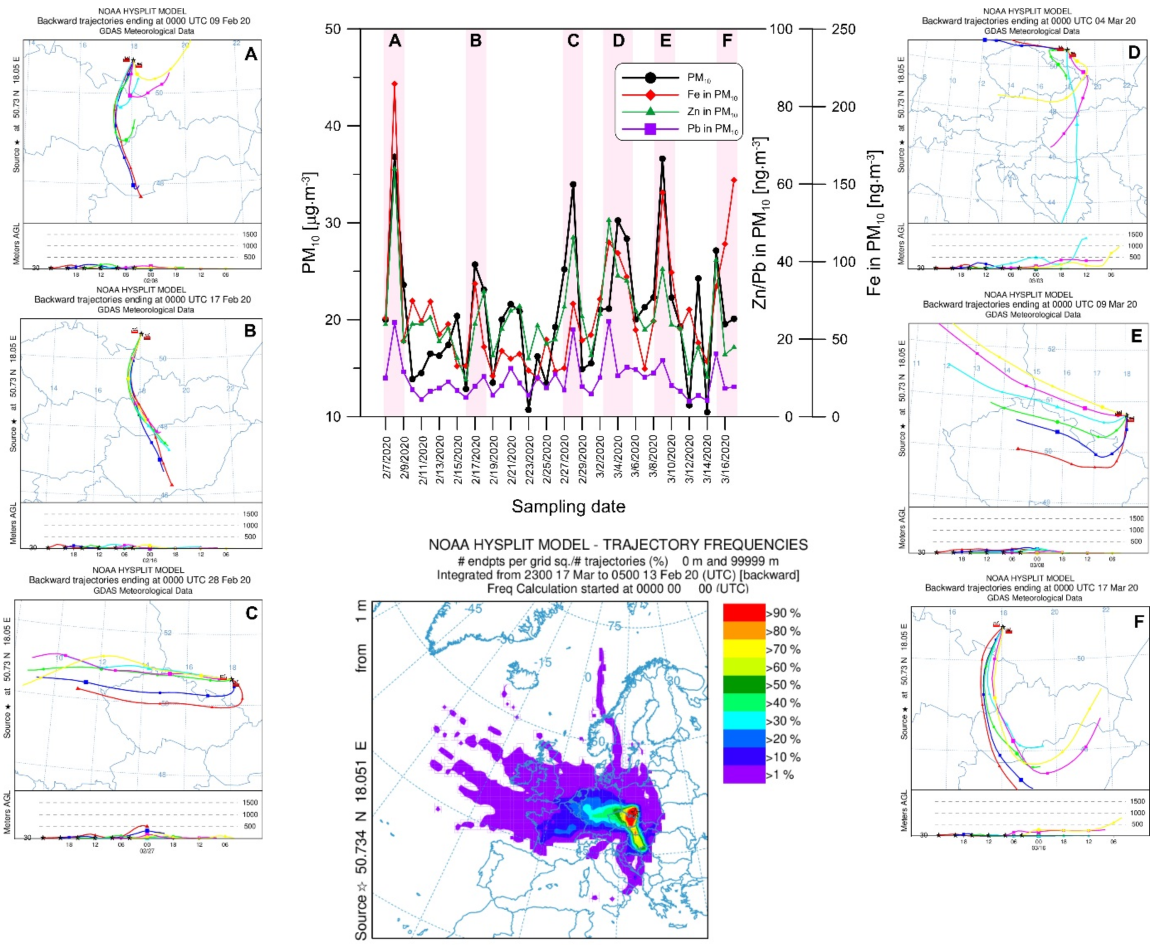

Figure 2. HYSPLIT trajectory frequencies and 24 h air backward trajectories in Kotórz calculated for given episodes (**A**–**F**).

6. Comparison of Methods

6.1. Concentration of PM-Bound Elements Obtained by Two Methods

The PM was sampled with the use of 10 spider webs and PM_{10} was collected by Horiba PX-375 CPM then the results from both methods were compared. Here we present the concentrations of selected elements in spider webs as violin plots (Figure 3). The horizontal coordinates of the violins are located at the positions corresponding to the concentrations measured with the Horiba PX-375. The values obtained by using CPM were intentionally recalculated to obtain the concentrations of given elements in PM_{10} and expressed in $mg \cdot kg^{-1}$. By this, the comparison of these results with particles adsorbed on spider webs was possible.

The amounts of accumulated PTEs in the case of both methods differed. Figure 3 shows that the most commonly accumulated element was Fe as well on spider web as in the results from CPM, while the least abundant was Cu also for both methods. Concentrations of Mn, Pb, and Zn revealed similar orders of magnitude for spider webs, but for Horiba PX-375 these values differed. In general, the order of accumulated elements for webs was as follows: Fe > Pb > Mn > Zn > Cu while for particulate monitor: Fe > Zn > Pb > Mn > Cu. However, for all PTEs (except Zn), the results obtained for spider webs were higher than for CPM. It needs to be remembered that the Horiba PX-375 CPM collected the selected PM_{10} fraction, which contains particles smaller than 10 µm while on the spider web also bigger particles are accumulated. There is also a possibility that fine particles bearing some elements will not be able to accumulate on web threads according to the threads arrangement (too big meshes).

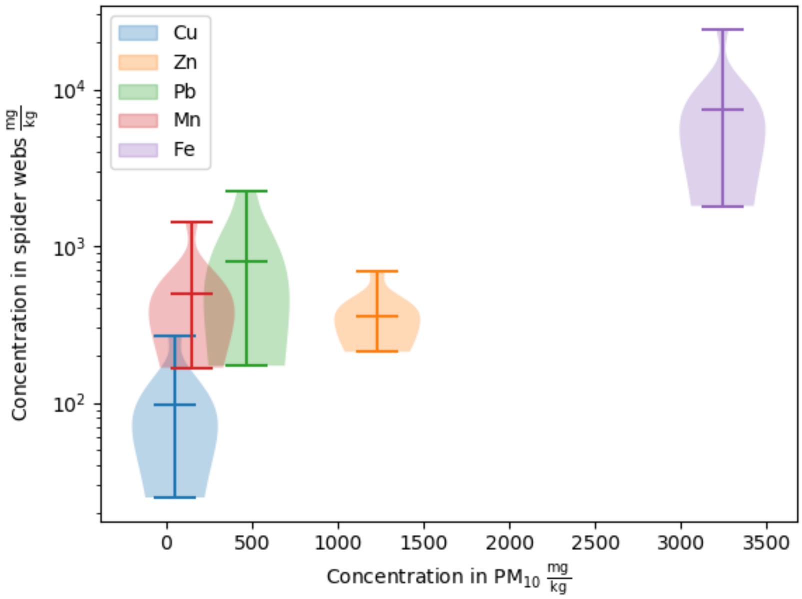

Figure 3. Concentrations in spider webs with relation to the concentration measured by Horiba PX-375. The horizontal position of the violin is the total concentration of PM_{10} while in the vertical direction the violin represents the distribution of concentration.

6.2. Percentage Contribution of Given Element

According to the fact that the exact number of concentrated elements for these two methods of air pollution monitoring varies due to different mechanisms responsible for PM collection, we wanted also to check the frequency of occurrence for selected metals in the total amount of studied atmospheric aerosols. For this purpose, obtained results for spider webs (expressed in µg/g; Table S2) and for CPM (in ng/m^3; Table S1) were converted into percentage contribution. As shown on the Figure 4, the view on the results in this manner enables the information about agreement of both methods given in percentage of difference. It can be noticed, that for Pb almost complete agreement was found, having about 10% share in both methods. In the case on Mn and Cu, their contribution in total aerosols was very small for both tools. There was about 30% difference in the answer between spider web and CPM for Mn, showing bigger Mn input on spider web, while Cu contribution differed in less than 50%, however its input in total metals is so small (about 1%) so that it is very hard to give precise answer. For the most abundant element, which was Fe, the result is satisfying, revealing about 25% difference between methods and bigger contribution of this element on spider webs. The highest difference was observed for Zn which was commonly found in the particles from CPM but its contribution on spider web was very poor. It resulted in bigger than 50% difference between these methods.

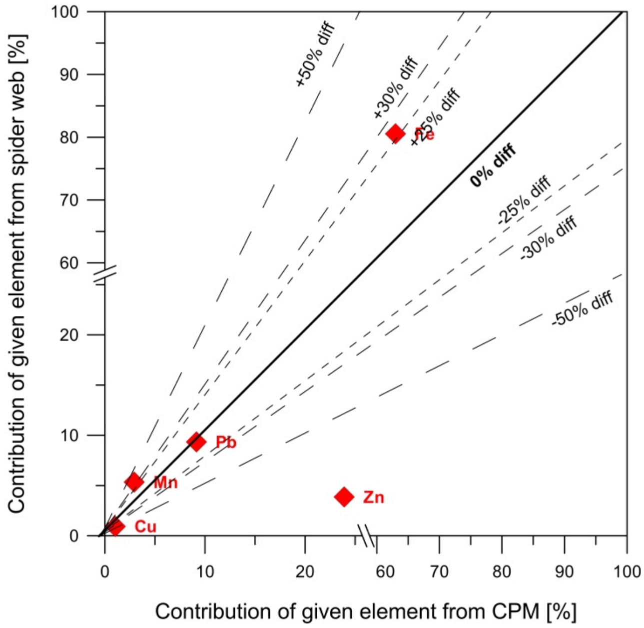

Figure 4. The comparison of both applied methods (spider web and CPM) for assessing the air pollution (% of difference).

7. Discussion

In the study by Olszowski [61] it was shown that the average mass concentrations of particulate matter were significantly higher in Kotórz Mały than in other rural regions in Poland and Czech Republic which indicates that the problem of air quality in the study area is relevant and current. Therefore, the dynamic situation in terms of air pollution in Poland, also in small villages, requires cheap, easy, and simple tools to monitor air quality. Considering that, we focused on validating the method of air pollution monitoring with the use of spider webs and its comparison with CPM.

The spider web is easily accessible, low cost and not complicated in use material [18]. What is more, monitoring with this indicator can be considered non-invasive and zero-waste as no extra waste is produced. Spider webs are supposed to collect total suspended particulate matter (TSP) and the obtained results could indicate the specific elements that seem to be problematic in the study area and give a simple overall and qualitative information whether more specific, more precise monitoring is needed. In order to check the reliability of the obtained results from spider web monitoring a comparison of our results with other studies was conducted. For the purposes of this article, the most relevant seems to be a comparison with the results obtained also in Poland and preferably with the use of the web produced by the same spider family. Additionally, the values of element concentrations were recalculated into a one-month exposition (Table 4), which allowed us to easily compare the obtained results. The elemental composition and the concentrations of specific elements varied depending on the study area. For instance, in the paper by Rybak [13] a similar experiment was conducted, however, the concentration of Fe was almost four times lower in there (7469 μg/g in this study, 2058 μg/g in paper by Rybak; Table 4) which can indicate much higher emission of this element in the area of Kotórz Mały due to close location of railway tracks and long-range transport (Figure 2). Moreover, the concentrations of Pb and Mn were a few times higher than reported for Wrocław [13] (Table 4). In the case of Zn, similar values were found in the present study and Stojanowska et al. [15] or Bartz et al. [17], however, when comparing it with the results from Wrocław we could notice an almost two times higher results for the study by Rybak [13] and nearly ten times higher value in the paper by Rybak et al. [18] which is not that surprising as three out of the five tested locations were located just right next to road with very intensive road traffic [18]. In addition, this might be a case in the study by Rybak [13]. Both of Rybak's studies were conducted in a big polish city characterized by heavy motor traffic.

On the other hand, the amount of collected Cu in the area of Kotórz is small, especially when compared to areas where copper smelting dominates [15,17] but the influence of Cu smelting in this region cannot be excluded. The observations of visibly higher Cu concentrations in areas with the proximity of Cu smelters and the information listed above prove that the spider web can be considered a good bioindicator. Hence, it can be concluded that this comparison of PTEs content on webs with other researches indicated that the results obtained in this study are reasonable. Additionally, elevated values for some elements can be easily explained by the analysis of the dominating sources of pollution in this area (Figure 2).

Table 4. Concentrations of average PTEs in this study and selected other researches (for easier comparison it was recalculated to one month of exposition).

Parameter	This Study	Stojanowska et al. (2020)	Rybak (2015)	Rybak et al. (2015)	Bartz et al. (2021)
Study area	Kotórz Mały	Smelter in Legnica	Wrocław	Wrocław	Smelter in Głogów
Fe [µg/g]	7469		2058		
Mn [µg/g]	494		146		
Pb [µg/g]	797	307	87	738 (2011) 790 (2012)	357
Zn [µg/g]	357	500	738	3666 (2011) 1919(2012)	479
Cu [µg/g]	98	706	109		226
Exposition time	1 month	1 month (recalculated from 2 months)	1 month (recalculated from 2 months)	1 month	1 month (recalculated from 3 months)

Aware of the fact that results obtained with CPM are very accurate it has to be remembered that it is rather an expensive device and its use is limited due to high costs. On the contrary, spider web is non-expensive, easily accessible material. Hence, the webs may seem in this case to be promising alternative for the air quality monitoring. Above mentioned confrontation of results verified that identified elements concentrations on webs are reasonable and could be suspected to comparison with CPM. As it is commonly known, CPM provide very precise information about PTEs concentrations and hence, as it presents the actual air pollution, it seems to be good point of reference for spider webs. It needs to be mentioned that the spider web was exposed to the air pollution, the same time in which CPM constantly worked. As presented on Figure 2, the results were recalculated to enable the comparison between these two methods and given in the total amount of selected elements in the whole sampling period. However, CPM collected only one selected fraction (PM_{10}), while on the spider web, also bigger particles were adsorbed and according to that the correlations were not found. What is more, finer particles could possibly not be able to accumulate on web threads as the threads arrangement is very specific (possibly too big meshes for some particles).

As presented in our research, noticeable amounts of chosen PTEs were found in the air samples, mostly revealing higher amounts for the particles collected on spider webs (Figure 3) with an exception for Zn. Both methods (CPM and spider web) clearly indicated that the most commonly found element was Fe, clearly distinguishable from the other elements. However, for Fe particles collected by CPM, only minimal enrichment in this element was found, hence its origin should be rather assigned to natural sources and occasionally to anthropogenic activities (long range transport as hypothesized based on Figure 2 or rail-wheel-brake interactions [12,56]). As a confirmation, in the paper by Mach et al. [62] also a low EF value (2.5 average for the period) was found, indicating rather natural sources of Fe in PM_{10} in this region. However, it needs to be remembered that the EF value was calculated based on the CPM results (reporting only PM_{10}). Observing the comparison of the Fe values collected on spider web in this study (rural area) and the other study conducted in urban area [13] it could be seen that the result here was much higher (Table 4). This is surprising but might only indicate that in this rural area there are some additional sources of Fe pollution as indicated by air backward trajectories (Figure 2). Since EF, based on CPM results, showed small enrichment in anthropogenic Fe it can be supposed that it probably occurred in the form of aggregates, which easily settled on the web threads but were not reported by CPM.

As mentioned above, Zn was the only element, which concentration was slightly higher in CPM results than in webs. It can be supposed that Zn was present in a big part in the fine fraction (similarly to the results from the study by Bartz et al. [17]) or even ultrafine fraction [63] which could complicate the accumulation on web due to too big meshes (specific threads arrangement) or the limitation of wet deposition. According to [64] some of finer fractions might be favorably deposited by wet deposition rather than that gravitational settling. Hence, as in this study the webs were protected from rain or snow, the wet deposition could be limited. As the EF showed extremely high enrichment in Zn, the impact of anthropopressure in this area is of much concern. The air masses with Zn can be transported from abroad, originating from steel manufacturing conurbation of Ostrava (Czech Republic) as it was shown by HYSPLIT trajectories (Figure 2). The emission of Zn in this can be also connected with polish industry pollution sources e.g., Cu smelting in Legnica and Głogów, from which Zn, co-appearing with Cu and Pb can be brought. However, the influence of vehicle emissions cannot be omitted as, since the time that leaded fuels were banned, it was chosen to be a new tracer of traffic emissions instead of Pb [65]. As additional sources of Zn, tailpipe emissions of motor oil [66] and tire wear [67] are considered. The sampling point (Figure 1) was located within a few kilometers of two national roads: Road No. 46 (southeast from the sampling point, approx. 9500 vehicles/day) and Road No. 45 (northwest from the sampling point, approx. 8000 vehicles/day) [68] and what is more, A4 highway, connecting east and west parts of southern Poland, pass through this region. Kotórz Mały lies about 80 km away from the most heavily loaded part of the route, which is in Katowice (100,983 vehicles/day) [68] and it is known to be a big source of Zn pollution [69]. Hence, the high value of EF for this element is not that surprising and the differentiation from spider webs results can be understood.

In the case of Pb, its concentration on spider web was also higher than reported by CPM. Even if the leaded fuel is not so commonly used anymore it seems that there is still a problem with the contamination by this element. This situation was confirmed by elevated EF value, indicating extremely high enrichment, and the fact that the results for spider webs, obtained in our study, exceeded the values from other studies (Table 4). Pb presence is often connected with high usage of motor vehicles in the urban area (i.e., lead wheel weights dropped from car wheels can be then pulverized by intensive traffic [70]. What is more, the origin of Pb particles in the air can be also connected with coal burning for home heating purposes, and it can be found in varying quantities in low-rank coals and high-rank coals and their corresponding ashes [71]. Combining this information with the fact that more than 90% of the households in the village use coal for heating processes [24] a big part of the identified pollution can be attributed to this sector. From the polish local sources, as a contributor to Pb emission, we can also mention A4 highway [69] and regions with Cu smelting (Legnica and Głogów) [32]. Another source of pollution with Pb in this area can be long range transport bringing pollution from steel manufacturing conurbation of Ostrava (Czech Republic) as shown in Figure 2.

Even if Cu was not that commonly found, comparing to other elements, neither on spider web nor in case of CPM sampling, the EF shows that the enrichment was very high (Table 3). This could be the result of bringing the pollution from the polish Cu smelting regions or Czech non-ferrous smelter in Príbram [37], as showed by air mass backward trajectories on Figure 2. Cu, as well as Zn, can be also a marker of brake lining wear [67,69] which could be the case here according to the fact of proximity of national roads and A4 highway. The presence of this element on spider webs shows similarity in term of quantity to results from Wrocław but observed amount was visibly lower than those from Cu smelting regions (Table 4). However, the impact of Cu smelters cannot be excluded, as particles from over there could be also brought in here but in smaller amounts.

In the case of Mn, the EF value was low indicating lower anthropogenic impact, hence the attention was focused on the other, more interesting, above-mentioned elements. As anthropogenic sources of Mn particles petrol combustion [72] and coal combustion in power plants [73] can be considered. On the other hand, in the natural environment, it also commonly occurs in most iron ores [74]. In this study, it was rather negligible and as showed by EF its origin could be mainly connected with natural processes.

Consideration of this study in terms of various elements and their origin helped us to explain the differences that could be noted while comparing the spider webs and CPM monitoring. What is more, the observed variance can be possibly connected with the different materials used in the case of spider web biomonitoring (natural product, protein) and CPM with PTFE membrane (fluoropolymer). Despite different materials in these two methods the similarity can be found in the structure as both of them are characterized by irregular structure of threads arrangement which creates tortuous routes through the material. As presented by Lindsley [75] these tortuous paths through which particles have to pass through greatly increase the probability of particle deposition. The observed differences may also result from different mechanisms responsible for particles accumulation. While for PTFE filters the accumulation mechanisms are well known (interception, impaction, diffusion, electrostatic attraction and sedimentation [75]) for spider webs it is more complicated. As it is considered a passive method sedimentation obviously occurs. It has been previously proposed that electrostatic forces could play an important role in silk adhesion [76,77] however experimental evidence concerning cribellar silk shows that it has non-electrostatic adhesive properties [78] after [79]. Then according to Vollrath and Edmonds [80] it is the specific glue that coats orb spider's webs which is responsible for electrostatic properties causing enhanced collection of charged particles (i.e., pollens, pollutants particles and flying insects). For instance, for orb webs the capture effectiveness is attributed to mechanical, adhesive, hygroscopic features of the constituent silk but also to architectural structure and the distortions of the entire structure induced by wind [78]. Apart from the fact that Agelenidae webs are non-sticky (not covered with glue) the rest of the mechanisms responsible for particles capture might be similar. According to this unclear situation, it is very difficult to compare these two materials.

Considering the different mechanisms occurring in these two methods (active method and biomonitoring-based passive method) it was expected that CPM could collect more particles. However, due to the selective collection of particles, and the other reasons mentioned above, the opposite situation was observed (generally higher PTEs in spider webs). Additionally, the percentage contribution of selected elements in total atmospheric particles, analyzed by us with the use of spider web and CPM, was presented (Figure 4). It was shown that only input of Zn in total amount of metals revealed no agreement between both methods (>50% difference). For the rest of elements, the difference between methods varied, giving 0–40% of difference. The most accurate result was obtained for Pb which showed almost complete agreement, indicating that even if the concentrations were different the percentage share in total aerosols was the same.

8. Conclusions

To summarize, spider webs and CPM can give satisfying results, but their comparison is not always clear due to different mechanisms of particles accumulation. It was shown that most elements concentrations, except Zn, were higher for spider webs indicating that some of the particles could occur in sizes bigger than PM_{10} due to formation of aggregates. As CMP collected only PM_{10}, these big aggregates were not reported and it lead to the differentiation of results between both methods. However, the percentage share of selected elements is very similar in both methods and the differences in the results are somehow understandable and can be explained considering the origin of the particles and the occurrence of given elements in different fractions. Additionally, we observed that the order of occurrence of elements was similar (at least in the case of the most abundant and the least abundant PTEs). In addition, obtained results are somehow comparable with other biomonitoring studies based on the use of spider webs which confirms the reliability of this results. This in turn, proves that this new bioindicator can be a good tool in air pollution monitoring. However, the issue needs to be studied in more details in the future and the correlation between PTEs in other fractions ($PM_{2.5}$ and especially TSP) obtained by active sampling and accumulation of PTEs on spider webs should be checked.

Supplementary Materials: The following are available online at https://www.mdpi.com/article/10.3390/min11080812/s1, Table S1: Results obtained in monitoring with the use of Continuous Particulate Monitor, Table S2: Results obtained in monitoring with the use of spider website, Table S3: Comparison of measured and certified concentrations in BCR-482 lichen.

Author Contributions: Conceptualization: A.S., T.M., T.O., J.R., M.G. and J.S.B.; methodology: T.M., M.R., P.Ś., J.S.B.; validation: A.S.; formal analysis: J.S.B., M.G. and A.S.; investigation: A.S., T.M., T.O., M.R. and P.Ś. resources: A.S., T.M., M.R. and P.Ś.; data curation: M.G. and J.S.B.; writing—original draft preparation, A.S.; writing—review and editing, T.O., J.R. and M.G.; visualization, M.G., J.S.B.; supervision, J.R.; project administration: J.R., A.S.; funding acquisition: J.R. and M.G. All authors have read and agreed to the published version of the manuscript.

Funding: This paper was co-financed within the "Excellent Science" program of the Polish Ministry of Science and Higher Education. This research was carried out as a part of the "Implementation doctorate-edition II Faculty W-7 (03DW/0001/18)" project, financed by the National Centre for Research and Development. The funders had no role in the design of the study, in the collection, analyses, or interpretation of data; in the writing of the manuscript, or in the decision to publish the results.

Ministry of Science and Higher Education
Republic of Poland

Institutional Review Board Statement: Not applicable.

Informed Consent Statement: Not applicable.

Acknowledgments: The authors gratefully acknowledge the NOAA Air Resources Laboratory (ARL) for the provision of the HYSPLIT transport and dispersion model and/or READY website (https://www.ready.noaa.gov accessed on 21 July 2021) used in this publication.

Conflicts of Interest: The authors declare no conflict of interest.

References

1. Ukaogo, P.O.; Ewuzie, U.; Onwuka, C.V. Environmental Pollution: Causes, Effects, and the Remedies. In *Microorganisms for Sustainable Environment and Health*, 1st ed.; Chowdhary, P., Raj, A., Vermna, D., Akhter, Y., Eds.; Elsevier: Amsterdam, The Netherlands, 2020; pp. 419–429.
2. Yadav, I.C.; Devi, N.L. Biomass Burning, Regional Air Quality, and Climate Change. In *Encyclopedia of Environmental Health*, 2nd ed.; Nriagu, J., Ed.; Elsevier: Amsterdam, The Netherlands, 2019; pp. 386–391.
3. European Environment Agency. *Air Quality in Europe—2019 Report*; European Environmental Agency: Copenhagen, Denmark, 2019.
4. World Health Organization. *Health Effects of Particulate Matter*; WHO: Geneva, Switzerland, 2013.
5. Braniš, M.; Domasová, M.; Řezáčová, P. Particulate air pollution in a small settlement: The effect of local heating. *Appl. Geochem.* **2007**, *22*, 1255–1264. [CrossRef]
6. Furusjö, E.; Sternbeck, J.; Cousins, A.P. PM10 source characterization at urban and highway roadside locations. *Sci. Total Environ.* **2007**, *387*, 206–219. [CrossRef] [PubMed]
7. Landrigan, P.J.; Fuller, R.; Acosta, N.J.R.; Adeyi, O.; Arnold, R.; Basu, N.N.; Baldé, A.B.; Bertollini, R.; Bose-O'Reilly, S.; Boufford, J.I.; et al. The Lancet Commission on pollution and health. *Lancet* **2018**, *391*, 462–512. [CrossRef]
8. Ciężka, M.M.; Górka, M.; Modelska, M.; Tyszka, R.; Samecka-Cymerman, A.; Lewińska, A.; Łubek, A.; Widory, D. The coupled study of metal concentrations and electron paramagnetic resonance (EPR) of lichens (Hypogymnia physodes) from the Świętokrzyski National Park—Environmental implications. *Environ. Sci. Pollut. Res.* **2018**, *25*, 25348–25362. [CrossRef] [PubMed]
9. Kłos, A.; Ziembik, Z.; Rajfur, M.; Dołhańczuk-Śródka, A.; Bochenek, Z.; Bjerke, J.W.; Tømmervik, T.; Zagajewski, B.; Ziółkowski, D.; Jerz, D.; et al. Using moss and lichens in biomonitoring of heavy-metal contamination of forest areas in southern and north-eastern Poland. *Sci. Total Environ.* **2018**, *627*, 438–449. [CrossRef] [PubMed]
10. Świsłowski, P.; Kosior, G.; Rajfur, M. The influence of preparation methodology on the concentrations of heavy metals in Pleurozium schreberi moss samples prior to use in active biomonitoring studies. *Environ. Sci. Pollut. Res.* **2021**, *28*, 10068–10076. [CrossRef]

11. Wang, L.; Gong, H.; Liao, W.; Wang, Z. Accumulation of particles on the surface of leaves during leaf expansion. *Sci. Total Environ.* **2015**, *532*, 420–434. [CrossRef]
12. Górka, M.; Bartz, W.; Rybak, J. The mineralogical interpretation of particulate matter deposited on Agelenidae and Pholcidae spider webs in the city of Wrocław (SW Poland): A preliminary case study. *J. Aerosol Sci.* **2018**, *123*, 63–75. [CrossRef]
13. Rybak, J. Accumulation of Major and Trace Elements in Spider Webs. *Water Air Soil Pollut.* **2015**, *226*, 1–12. [CrossRef] [PubMed]
14. Rybak, J.; Sówka, I.; Zwoździak, A. Preliminary assessment of use of Spider webs for the indication of air contaminants. *Environ. Prot. Eng.* **2012**, *38*, 175–181. [CrossRef]
15. Stojanowska, A.; Rybak, J.; Bożym, M.; Olszowski, T.; Bihałowicz, J.S. Spider webs and lichens as bioindicators of heavy metals: A comparison study in the vicinity of a copper smelter (Poland). *Sustainability* **2020**, *12*, 8066. [CrossRef]
16. Xiao-Li, S.; Yu, P.; Hose, G.C.; Jian, C.; Feng-Xiang, L. Spider webs as indicators of heavy metal pollution in air. *Bull. Environ. Contam. Toxicol.* **2006**, *76*, 271–277. [CrossRef] [PubMed]
17. Bartz, W.; Górka, M.; Rybak, J.; Rutkowski, R.; Stojanowska, A. The assessment of effectiveness of SEM- EDX and ICP-MS methods in the process of determining the mineralogical and geochemical composition of particulate matter deposited on spider webs. *Chemosphere* **2021**, *278*, 130454. [CrossRef]
18. Rybak, J.; Sówka, I.; Zwozdziak, A.; Fortuna, M.; Trzepla-Nabagło, K. Evaluation of the Usefulness of Spider Webs as an Air Quality Monitoring Tool for Heavy Metals. *Ecol. Chem. Eng.* **2015**, *22*, 400. [CrossRef]
19. Rybak, J.; Rogula-Kozłowska, W.; Loska, K.; Widziewicz, K.; Rutkowski, R. The concentration of Cu and Pb in the funnel spider Eratigena atrica (CL Koch 1843) (Araneae: Agelenidae) and its web. *Chem. Ecol.* **2019**, *35*, 1–12. [CrossRef]
20. Rybak, J.; Olejniczak, T. Accumulation of polycyclic aromatic hydrocarbons (PAHs) on the spider webs in the vicinity of road traffic emissions. *Environ. Sci. Pollut. Res.* **2014**, *21*, 2313–2324. [CrossRef]
21. Rybak, J.; Rogula-Kozłowska, W.; Jureczko, I.; Rutkowski, R. Monitoring of indoor polycyclic aromatic hydrocarbons using spider webs. *Chemosphere* **2019**, *218*, 758–766. [CrossRef] [PubMed]
22. van Laaten, N.; Merten, D.; von Tümpling, W.; Schäfer, T.; Pirrung, M. Comparison of Spider Web and Moss Bag Biomonitoring to Detect Sources of Airborne Trace Elements. *Water Air Soil Pollut.* **2020**, *231*, 1–17. [CrossRef]
23. Regionalny Wydział Monitoringu Środowiska w Opolu. *Roczna Ocena Jakości Powietrza w Województwie Opolskim—Raport Wojewódzki za Rok 2019*; Regionalny Wydział Monitoringu Środowiska w Opolu: Opole, Poland, 2020.
24. Olszowski, T. The concentration of PM10 in a rural area during episodes of tropospheric inversion occurring in the cool months. *ProScience* **2014**, *1*, 387–392.
25. European Environment Agency. *Costs of Air Pollution from European Industrial Facilities 2008–2012—An Updated Assessment. EEA Technical Report No 20/2014*; European Environmental Agency: Copenhagen, Denmark, 2014.
26. WIOŚ. *Raport o Stanie Środowiska Województwa Dolnośląskiego w 2007*; WIOS: Wrocław, Poland, 2008.
27. Parzentny, H.R.; Róg, L. Potentially hazardous trace elements in ash from combustion of coals in limnic series (Upper Carboniferous) of the Upper Silesian Coal Basin. *Górnictwo Geol.* **2007**, *3*, 81–91.
28. Srogi, K. Pierwiastki śladowe w węglu. *Wiadomości Górnicze* **2007**, *2*, 87–96.
29. Wierońska, F.; Makowska, D.; Strugała, A.; Bytnar, K. Analysis of the Content of Nickel, Chromium, Lead and Zinc in Solid Products of Coal Combustion (CCPs) Coming From Polish Power Plants. In *IOP Conference Series: Earth and Environmental Science*; IOP Publishing: Bristol, UK, 2019.
30. Widera, M.; Kasztelewicz, Z.; Ptak, M. Lignite mining and electricity generation in Poland: The current state and future prospects. *Energy Policy* **2016**, *92*, 151–157. [CrossRef]
31. Czech, T.; Marchewicz, A.; Sobczyk, A.T.; Krupa, A.; Jaworek, A. Śliwiński, Ł.; Rosiak, D. Heavy metals partitioning in fly ashes between various stages of electrostatic precipitator after combustion of different types of coal. *Process. Saf. Environ. Prot.* **2020**, *133*, 18–31. [CrossRef]
32. Muszer, A. *Charakterystyka Sferul i Minerałów Akcesorycznych z Wybranych Utworów Fanerozoicznych i Antropogenicznych*; Fundacja Ostoja: Wrocław, Poland, 2007.
33. Podgórska, B.; Synowiec, P.; Górniak, J.; Podgórska, S. *Program Ochrony Środowiska dla Gminy Ozimek na Lata 2017–2020 wraz z Perspektywą na Lata 2021–2024*; ALBEKO: Opole, Poland, 2017.
34. Hanculak, J.; Kurbel, T.; Spaldon, T.; Sestinova, O.; Findorakova, L.; Fedorova, E. Influence of Iron and Steel Industry on Selected Elements of Atmospheric Deposition in the Urban and Suburban Area of Košice (Slovakia). *J. Pol. Miner. Eng. Soc.* **2005**, *16*, 95–102. [CrossRef]
35. Sýkorová, B.; Kucbel, M.; Raclavská, H.; Raclavský, K.; Matýsek, D. Heavy metals in air nanoparticles in affected industry area. *J. Sustain. Dev. Energy Water Environ. Syst.* **2017**, *5*, 58–68. [CrossRef]
36. Hykyšová, S.; Brejcha, J. Monitoring of PM10 air pollution in small settlements close to opencast mines in the North-Bohemian Brown Coal Basin. *WIT Trans. Ecol. Environ.* **2009**, *123*, 387–398. [CrossRef]
37. Suchara, I.; Sucharová, J. Distribution of sulphur and heavy metals in forest floor humus of the Czech Republic. *Water Air Soil Pollut.* **2002**, *136*, 289–316. [CrossRef]
38. GIOŚ. *The State of the Environment in the Opolskie Voivodship*; GIOŚ: Opole, Poland, 2020. (In Polish)
39. HORIBA. New Construction Resolves Many of the Problems Associated with the Demanding Usage Environment for PM Sampling Filters. Available online: http://www.horiba.com/fileadmin/uploads/Process-Environmental/Documents/Downloads_Catalog/Catalog_Ambient/TFH-01_47_brochure_HRE2423B_uploaded_on_20140619.pdf (accessed on 20 June 2021).

40. Zhang, Y.; Yin, M.; Xia, O.; Zhang, A.P.; Tam, H.Y. Optical 3D µ-printing of polytetrafluoroethylene (PTFE) microstructures. In Proceedings of the IEEE International Conference on Micro Electro Mechanical Systems (MEMS), Belfast, Northern Ireland, 21–25 January 2018; pp. 37–40.
41. Ebnesajjad, S. Introduction to Fluoropolymers: Materials, Technology, and Applications. In *Introduction to Fluoropolymers: Materials, Technology, and Applications*; Elsevier LTD: Oxford, UK, 2013.
42. Teng, H. Overview of the development of the fluoropolymer industry. *Appl. Sci.* **2012**, *2*, 496–512. [CrossRef]
43. Liberti, A. Modern methods for air pollution monitoring. *Pure Appl. Chem.* **1975**, 519–534. [CrossRef]
44. Rolph, G.; Stein, A.; Stunder, B. Real-time Environmental Applications and Display sYstem: READY. *Environ. Model. Softw.* **2017**, *95*, 210–228. [CrossRef]
45. Stein, A.F.; Draxler, R.R.; Rolph, G.D.; Stunder, B.J.B.; Cohen, M.D.; Ngan, F. Noaa's hysplit atmospheric transport and dispersion modeling system. *Bull. Am. Meteorol. Soc.* **2015**, *96*, 2059–2077. [CrossRef]
46. Zoller, W.H.; Gladney, E.S.; Duce, R.A. Atmospheric concentrations and sources of trace metals at the South Pole. *Science* **1974**, *183*, 198–200. [CrossRef] [PubMed]
47. Wedepohl, K.H. The composition of the continental crust. *Geochim. et Cosmochim. Acta* **1995**, *59*, 1217–1239. [CrossRef]
48. Yongming, H.; Peixuan, D.; Junji, C.; Posmentier, E.S. Multivariate analysis of heavy metal contamination in urban dusts of Xi'an, Central China. *Sci. Total Environ.* **2006**, *355*, 176–186. [CrossRef]
49. Al-Azawii, Z.N. Study on chemical composition and designing web patterns of Iraqi spider silk. *Biochem. Cell. Arch.* **2020**, *20*, 1397–1400. [CrossRef]
50. Hose, G.C.; James, J.M.; Gray, M.R. Spider webs as environmental indicators. *Environ. Pollut.* **2002**, *120*, 725–733. [CrossRef]
51. Gerboles, M.; Buzica, D.; Brown, R.J.C. Interlaboratory comparison exercise for the determination of As, Cd, Ni and Pb in PM_{10} in Europe. *Atmos. Environ.* **2011**, *45*, 3488–3499. [CrossRef]
52. Konopka, Z.; Swisłowski, P.; Rajfur, M. Biomonitoring of Atmospheric Aerosol with the use of Apis mellifera and Pleurozium schreberi. *Chem. Didact. Ecol. Metrol.* **2020**, *24*, 107–116. [CrossRef]
53. Spectro-Lab. *Instrukcja Obsługi Aparatu AAS iCE 3500 Firmy Thermo Scientific*; Spectro-Lab: Warszawa, Poland, 2013.
54. Tychowska-Jankowska, A. *Environmental Impact Forecast*; Burmistrz Ozimka: Ozimek, Poland, 2013. (In Polish). Available online: https://ozimek.pl/static/img/k01/obwieszczenia_burmistrza/2013/04_Prognoza_oddzialywania_na_srodowisko.pdf (accessed on 20 June 2021).
55. Muránszky, G.; Ovari, M.; Virág, I.; Csiba, P.; Dobai, R.; Záray, G. Chemical characterization of PM10 fractions of urban aerosol. *Microchem. J.* **2011**, *98*, 1–10. [CrossRef]
56. Byeon, S.H.; Willis, R.; Peters, T.M. Chemical characterization of outdoor and subway fine (PM2.5–1.0) and coarse (PM10–2.5) particulate matter in Seoul (Korea) by computer-controlled scanning electron microscopy (CCSEM). *Int. J. Environ. Res. Public Health* **2015**, *12*, 2090–2104. [CrossRef]
57. Nalbandian, H. *Trace Element Emissions from Coal*; IEA Clean Coal Centre: Paris, France, 2012. Available online: https://usea.org/sites/default/files/092012_Trace%20element%20emissions%20from%20coal_ccc203.pdf (accessed on 20 June 2021).
58. Vossler, T.; Cernikovsky, L.; Novak, J.; Placha, H.; Krejci, B.; Nikolova, I.; Chalupnickova, E.; Williams, R. An investigation of local and regional sources of fine particulate matter in Ostrava, the Czech Republic. *Atmos. Pollut. Res.* **2015**, *6*, 454–463. [CrossRef]
59. Pokorná, P.; Hovorka, J.; Klán, M.; Hopke, P.K. Source apportionment of size resolved particulate matter at a European air pollution hot spot. *Sci. Total Environ.* **2015**, *502*, 172–183. [CrossRef]
60. Slovak Hydrometeorological Institute. *Air Pollution in the Slovak Republic*; Slovak Hydrometeorological Institute: Bratislava, Slovakia, 2019.
61. Olszowski, T. Influence of individual household heating on PM2.5 concentration in a rural settlement. *Atmosphere* **2019**, *10*, 782. [CrossRef]
62. Mach, T.; Rogula-Kozłowska, W.; Bralewska, K.; Majewski, G.; Rogula-Kopiec, P.; Rybak, J. Impact of Municipal, Road Traffic, and Natural Sources on PM10: The Hourly Variability at a Rural Site in Poland. *Energies* **2021**, *14*, 2654. [CrossRef]
63. Juda-Rezler, K.; Kowalczyk, D. Size distribution and trace elements contents of coal fly ash from pulverized boilers. *Pol. J. Environ. Stud.* **2013**, *22*, 25–40.
64. Miler, M.; Gosar, M. Assessment of metal pollution sources by SEM/EDS analysis of solid particles in snow: A case study of Žerjav, Slovenia. *Microsc. Microanal.* **2013**, *19*, 1–14. [CrossRef] [PubMed]
65. Goix, S.; Resongles, E.; Point, D.; Oliva, P.; Duprey, J.L.; de la Galvez, E.; Ugarte, L.; Huayta, C.; Prunier, J.; Zouiten, C.; et al. Transplantation of epiphytic bioaccumulators (Tillandsia capillaris) for high spatial resolution biomonitoring of trace elements and point sources deconvolution in a complex mining/smelting urban context. *Atmos. Environ.* **2013**, *80*, 330–341. [CrossRef]
66. Cadle, S.H.; Mulawa, P.A.; Hunsanger, E.C.; Nelson, K.; Ragazzi, R.A.; Barrett, R.; Gallagher, G.L.; Lawson, D.R.; Knapp, K.T.; Snow, R. Composition of light-duty motor vehicle exhaust particulate matter in the Denver, Colorado area. *Environ. Sci. Technol.* **1999**, *33*, 2328–2339. [CrossRef]
67. Pant, P.; Harrison, R.M. Estimation of the contribution of road traffic emissions to particulate matter concentrations from field measurements: A review. *Atmos. Environ.* **2013**, *77*, 78–97. [CrossRef]
68. GDDKiA. *Generalny Pomiar Ruchu w 2015 Roku*; GDDKiA: Warsaw, Poland, 2016. (In Polish)
69. Adamiec, E.; Jarosz-Krzemińska, E.; Wieszała, R. Heavy metals from non-exhaust vehicle emissions in urban and motorway road dusts. *Environ. Monit. Assess.* **2016**, *188*, 369. [CrossRef]

70. Root, R.A. Lead loading of urban streets by motor vehicle wheel weights. *Environ. Health Perspect.* **2000**, *108*, 937. [CrossRef]
71. Bartoňová, L.; Raclavská, H.; Čech, B.; Kucbel, M. Behavior of Pb during coal combustion: An overview. *Sustainability* **2019**, *11*, 6061. [CrossRef]
72. Moore, K.; Polidori, A.; Sioutas, C. *Toxicological Assessment of Particulate Emissions From the Exhaust of Old and New Model Heavy- and Light-Duty Vehicles*; METRANS: Los Angeles, CA, USA, 2011.
73. Deng, S.; Shi, Y.; Liu, Y.; Zhang, C.; Wang, X.; Cao, Q.; Zhang, F. Emission characteristics of Cd, Pb and Mn from coal combustion: Field study at coal-fired power plants in China. *Fuel Process. Technol.* **2014**, *126*, 469–475. [CrossRef]
74. WHO. Chapter 6.8—Manganese. In *Air Quality Guidelines*, 2nd ed.; WHO: Geneva, Switzerland, 2001; pp. 1–13.
75. Lindsley, W.G. Filter Pore Size and Aerosol Sample Collection. In *NIOSH Manual of Analytical Methods*, 5th ed.; Kevin, A., O'Connor, P.F., Eds.; National Institute for Occupational Safety and Health: Washington, DC, USA, 2016; pp. 2–14.
76. Opell, B.D. What forces are responsible for the stickiness of spider cribellar threads? *J. Exp. Zool.* **1993**, *265*, 469–476. [CrossRef]
77. Opell, B.D. Do static electric forces contribute to the stickiness of a spider's cribellar prey capture threads? *J. Exp. Zool.* **1995**, *273*, 186–189. [CrossRef]
78. Ortega-Jimenez, V.M.; Dudley, R. Spiderweb deformation induced by electrostatically charged insects. *Sci. Rep.* **2013**, *3*, 1–4. [CrossRef] [PubMed]
79. Peters, H.M. The spinning apparatus of Uloboridae in relation to the structure and construction of capture threads (Arachnida, Araneida). *Zoomorphology* **1984**, *104*, 96–104. [CrossRef]
80. Vollrath, F.; Edmonds, D. Consequences of electrical conductivity in an orb spider's capture web. *Naturwissenschaften* **2013**, *100*, 1163–1169. [CrossRef] [PubMed]