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Magnetic Susceptibility of Spider Webs and Dust: Preliminary Study in Wrocław, Poland

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Abstract: Previous studies have proven that spider webs can be a reliable tool for magnetic biomonitoring. This study aims to present the magnetic susceptibility values of urban road dust (URD) settled indoors and outdoors, and compare these values with spider webs exposed to indoor and outdoor pollutants, and therefore to discuss their potential environmental implications. The webs of *Eratigena atrica*, *Tegenaria ferruginea*, and *Agelena labyrinthica* (Agelenidae) spiders from outdoor and indoor study sites were investigated, along with dust deposited on filters (indoors) and dust collected from the surrounding neighborhood (outdoors). Magnetic measurements revealed elevated levels of magnetic pollutants at all investigated sites in the city of Wrocław. The indoor/outdoor ratios of mass-specific magnetic susceptibility for the studied samples suggested a prevalence of indoor pollution sources at two of the sites (prosthetic laboratory and environmental science laboratory), whereas the third site (tenement house neighborhood) was dominated by material that presumably originated from predominantly outdoor sources. The indoor/outdoor ratios of magnetic susceptibility for the investigated matrices at the examined sites were highly comparable, which is promising for the utilization of spider webs in magnetic monitoring.

Keywords: spider webs; Agelenidae; magnetic susceptibility; pollution; dust; indoor; outdoor

1. Introduction

Settled particulate matter is derived from various sources, including soil (crustal material), vehicle emissions, coal combustion, industrial combustion, and biomass burning. These outdoor pollutants significantly influence indoor air quality. The indoor/outdoor particulate matter (PM) relationship is an important parameter for assessing the impact of PM on human health in urban areas. Therefore, constant monitoring of indoor and outdoor air quality is performed on demand, although conducting long-term monitoring studies based on detailed and direct measurements of PM concentrations is very expensive and demanding [1]. Hence, fast, reliable, and cost-efficient methods are always desirable. One such method for the qualitative assessment of environmental pollution levels is magnetometry. This method is based on the presumption that pollutants are accompanied by a fraction of strongly magnetic Fe-containing particulate matter [2]. Different environmental materials, such as dust (atmospheric total suspended particles, particulate matter (PM), road dust) and soil, in addition to living organisms, such as plants, lichens, and mosses, exhibit enhanced magnetic signals; therefore, they can be applied in environmental pollution studies using magnetometry. The vegetation growing in polluted areas is applied as a passive bioindicator of atmospheric pollution, with its magnetic properties reflecting the pollution level [3]. Urban road dust (URD) has also been used for the assessment of contamination levels in big cities [4].

Initially, most studies in the field of environmental magnetism were performed using pumped-air filters [5–9]. Previous studies have focused on outdoor pollution. The magnetic properties of PM deposited on filters have been examined mainly to identify industrial and traffic pollution [10]. Other studies have focused on the passive deposition of indoor or outdoor settled dust (e.g., by surface brushing) [10–13]. A few studies have been based on self-designed passive and non-selective PM samplers (e.g., small filter bags with natural wool sorbents), which can be compared to biological exposure [14].

In recent decades, biological materials have also been used in environmental magnetism studies. Magnetic biomonitoring has been proven to be an effective and inexpensive tool, providing qualitative or semiquantitative information on the magnetic properties of airborne PM.

The most commonly used materials include mosses and lichens, plant leaves, tree bark, trunk wood, insects, crustaceans, and mammal tissues [15]. Biological indicators such as spiders and their webs are of interest, because they provide reliable information on the state of the environment, similar to other bioindicators such as mosses and lichens [16,17]. Various pollutants, e.g., heavy metals and organic compounds, settle easily on spider webs at concentrations that are reliable for chemical analysis. The results from several studies have identified spider webs as excellent bioindicators [18–23]. However, only one of these studies was related to magnetic biomonitoring, leaving this area largely unexplored [23]. The presented study involved the investigation of silk made by four types of spiders: *Pholcus phalangioides* (Pholcidae), *Eratigena atrica*, *Agelena labyrinthica* (Agelenidae), and *Linyphia triangularis* (Linyphiidae). Increases in magnetic susceptibility observed for samples collected from both indoor and outdoor environments indicated contamination by anthropogenic pollutants containing ferromagnetic iron minerals. The study revealed that spider silk is capable of capturing particulate matter in a manner equivalent to flora-based bioindicators, such as mosses, lichens, or tree leaves. In addition, spider webs lack the limitations of other bioindicators. Spider webs are non-selective climate- and season-independent indicators, allowing for long-exposure monitoring (webs weaved by spiders can be used in the laboratory and stretched on Petri dishes).

The application of spider silk in the magnetic monitoring of urban road dust has never been directly compared to conventional methods. This study aims to report the magnetic susceptibility of urban road dust settled in indoor and outdoor environments, and to compare the data with results obtained from spider webs exposed to indoor and outdoor pollutants. The research hypothesis states that spider webs are appropriate substrates for monitoring environmental pollution due to their good entrapment of aeolian particulate pollution, and thus, they can be employed in studies of urban pollution pathways and human exposure to pollutants. Additionally, road dust represents an equilibrium of deposition and erosion since the last rain, wind, or storm event. Thus, we can assume that spider webs can re-disperse aeolian dusts in a linear and proportionate way, similar to stratigraphic layers of sediment on a road, allowing relationships to be established between webs and road dust and between indoor and outdoor sediments.

2. Materials and Methods

2.1. Study Area

The study was conducted in Wrocław, the largest city in south-west Poland, in Lower Silesia. All samples were collected at three sites located in different neighborhoods (denoted S, PG, and K) (Figure 1). Site S (Siemiradzkiego st.) was situated in a very quiet area of Wroclaw, with a small number of municipal sources of air pollutants (i.e., exhaust and non-exhaust emission from road traffic, stoves); site PG was in Grunwaldzki Square, a centrally located main interchange with heavy motor traffic; and site K (Kamieńskiego st.) was located in a prosthetic laboratory situated near a moderately busy road, surrounded by other service facilities and new tenement houses. A detailed description of the sites is presented in Table 1.

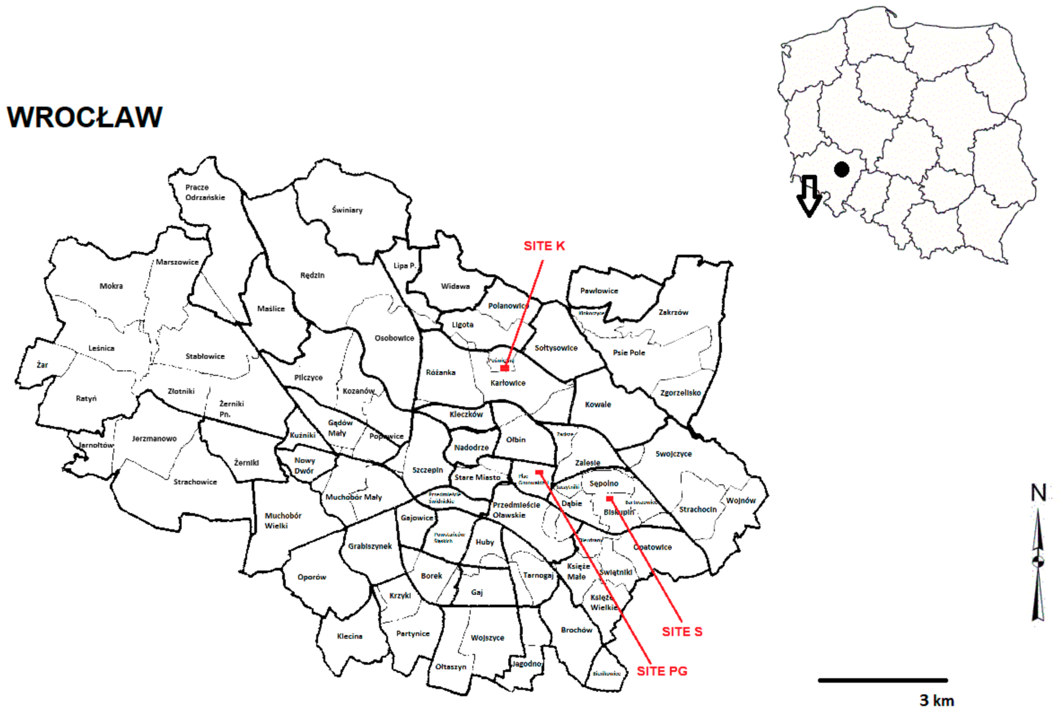

Figure 1. Map of Wrocław showing the three study sites (K, PG, and S). Map source: Creative Commons License (CC).

Table 1. A detailed description of studied sites and sampling matrices.

Name of Site	Site	Coordinates	Samples
S	Siemiradzkiego st. (Śródmieście district). Outdoor: tenement house neighborhood. Indoor: room (gas heating located in the kitchen) without smoking residents (number of inhabitants: 3).	51°06′04.2″ N 17°05′41.0″ E	Outdoor: *T. ferruginea* webs (n = 4), URD (*n* = 4). Indoor: *E. atrica* webs (n = 4), filters (n = 4).
PG	Grunwaldzki Square. Outdoor: the city center; bushes near the university building (height 0.5 m). Indoor: the environmental laboratory in a building belonging to Wrocław University of Science and Technology.	51°06′36.5″ N 17°03′25.1″ E	Outdoor: *A. labyrinthica* webs (*n* = 4), URD (*n* = 4). Indoor: *E. atrica* webs (*n* = 4), filters (n = 4).
K	Kamieńskiego st. Outdoor: outside of the prosthetic laboratory; bushes near the laboratory (height 0.5 m). Indoor: room where all types of prosthetic work are prepared (dentures, implants, etc.)	51°09′15.9″ N 17°02′39.1″ E	Outdoor: *A. labyrinthica* webs (*n* = 4), URD (*n* = 4). Indoor: *E. atrica* webs (*n* = 4), filters (*n* = 4).

2.2. Spider Characteristics

Three species of spiders belonging to the Agelenidae family were used for studies: *Eratigena atrica* (C.L. Koch, 1843), *Tegenaria ferruginea* (Panzer), and *Agelena labyrinthica* (Clerck, 1757). All of these spiders weave the same type of web, which is characteristic of all family members (Agelenidae). Because of this web shape, these spiders are called funnel web spiders, because the web consists of a sheet web with a funnel or tubular retreat where the spider waits for the prey. The web is composed of entirely dry silk. More importantly, the behavior of Agelenids is different from some Araneae representatives, which eat their old web before building a new one [24]. The non-stickiness of this type of web allows it to easily catch pollutants, particularly dust, because the web structure is very dense, firm, and compact. It was proven previously that these types of webs are excellent tools in the biomonitoring of air pollutants [21,22]. *Eratigena atrica* is a giant house spider that mainly lives in darker sites near people's houses; it can easily be found in the dark corners of basements. *Agelena labyrinthica* lives in vegetation, e.g., hedges and bushes. *Tegenaria ferruginea* lives in both habitats, and can be encountered near the ground, in forests, and also in buildings [25].

2.3. Sample Collection

The experiment was conducted from the beginning of May to the end of June 2018 (8 weeks). We collected four set of samples, each over a two week period. This period was characterized by average weather conditions of high temperature, light to moderate wind, and occasional rain showers. We collected four types of samples: outdoor urban road dust samples (OD); outdoor spider webs (OSW); indoor spider webs (ISW), which were collected with glass vials and glass rods to avoid contamination; and indoor dust (ID) collected passively on filters. One OD sample was collected every 2 days from the initially defined area measuring 25 cm × 30 cm (750 cm^2). On the first day of sample collection the area was cleaned; then, on every even day of the experiment period, a sample was collected using a portable vacuum cleaner fitted with an empty filter bag. All 7 samples covering the two week period were mixed and homogenized and treated as one sample. The procedure was to repeated for the second and remaining periods, involving cleaning of the same surface. The location of the area was nearest to the indoor sampling point. During the indoor sampling of dust (ID), we installed four filters measuring 150 mm in diameter (706.5 cm^2 in total). Two filters were installed on the interior sill in the room closest to the OD sampling point. The remaining two filters were placed on furniture at a similar height to the window sill, located in the same room. The OD and ID filter bags were weighed before and after sampling with a microbalance.

When sampling outdoors (OSW), we mainly used the naturally occurring webs belonging to these three spiders from the same family (they do not differ from each other). Therefore, before exposing outdoor webs to pollutants, old webs were removed. We collected only the new web construction, which was exposed for 8 weeks. Rarely, when it was not possible to find a natural web, we used already woven webs obtained from the laboratory rearing of *E. atrica*. Webs were stretched on Petri dishes and exposed to pollutants. Indoor clean webs were obtained via continuous laboratory breeding only (webs of *E. atrica).* Additionally, the above-described method had been used previously with success [26]. Indoor dust samples were exposed simultaneously on horizontal filter paper and webs at the same time and place. All samples were stored in dark containers in a refrigerator prior to analysis. The details of the samples are shown in Table 1.

2.4. Analytical Procedures

The collected web samples, after being cleaned to remove accidental artefacts, were dried (to constant mass), placed in 1 cm^3 plastic vials, weighed, and subjected to magnetic susceptibility (k) measurements using an MFK1 Kappabridge device (Agico Advanced Geoscience Instruments Co., Brno, Czech Republic) that operated at a low frequency (976 Hz) and low field intensity (200 A/m). Each sample was measured at least five times, and then the mean value was calculated. Subsequently, the mass-specific magnetic susceptibility (χ, m^3/kg) was computed by taking into account the weight of the samples. The magnetic susceptibility of the clean webs was measured and was negative, suggesting that they had diamagnetic properties; therefore, clean webs were used as reference samples.

2.5. Statistics

Because our study is preliminary and presents some of the first results in this field, we are aware that statistical analysis should be conducted carefully; however, we wanted to show this method of comparative analysis of the magnetic susceptibility of samples from spider webs and dust. The number of samples was not large (four samples in series); however, during the sample preparation procedure, the homogenization process meant that in fact each value of χ for the outdoor samples was an estimate obtained from seven samples, and for indoor samples each estimate was obtained from four samples. This allowed us to perform basic statistical analysis (the true number of samples was greater than four). To test whether the data were normal, the Shapiro–Wilk test was used for normality [27]. Sets containing four data points were tested separately for every site and type of sample: outdoor and indoor spider webs, urban road dust, and indoor settled dust on filters. We investigated whether any two samples collected at a given site, or any two samples collected using the same technique at different sites, differed from each other. Depending on the result of the Shapiro–Wilk test, Welch's t-test [28] or the Wilcoxon signed-rank test [29] was used to test the difference between samples. If both samples passed the Shapiro–Wilk test, Welch's t-test was applied, because the assumptions of this test were fulfilled. If the normality of any of two tested samples had to be rejected, then we used the Wilcoxon test. The values are presented as matrices of *p*-values in the Supplementary Material. The hypothesis testing limits for the statistics we calculated in the tests above were very high because we used four element samples. Then, the Spearman or Pearson coefficient of correlation between these samples was calculated [30]. The decision of whether to use the Spearman or Pearson coefficient was taken analogously to the Wilcoxon test and Welch's t-test. We would like to extend our statistical analysis; however, conducting further analysis will most probably lead to unjustified results.

For such small samples, it was likely that the variances were relatively high. The uncertainties of the ratio were calculated with the non-linear (few terms) Taylor expansion of the function $f(x, y)$. Uncertainties calculated in such a way do not have to be symmetrical. We evaluated the maximum and minimum possible uncertainties values separately. For $f(x, y)$:

$$\Delta f^{+} = \max(f(x \pm \Delta x, y \pm \Delta y)) - f(x, y), \tag{1}$$

$$\Delta f^{-} = f(x, y) - \min(f(x \pm \Delta x, y \pm \Delta y)), \tag{2}$$

where Δf^{+} and Δf^{-} are maximum and minimum possible values, respectively, obtained in the Taylor expansion of the function for $+\Delta x$ or $-\Delta x$ and $+\Delta y$ or $-\Delta y$. We expanded the functions up to the fifth order according to the following formula:

$$f(x+\Delta x, y+\Delta y) = f(x,y) + \frac{\partial f}{\partial x}\cdot\Delta x + \frac{\partial f}{\partial y}\cdot\Delta y + \frac{\partial^2 f}{\partial x^2}\cdot\frac{(\Delta x)^2}{2} + \frac{\partial^2 f}{\partial y^2}\cdot\frac{(\Delta y)^2}{2} + \frac{\partial^2 f}{\partial x \partial y}\cdot\frac{\Delta x \Delta y}{2} + \dots. \tag{3}$$

The statistics analysis was undertaken using Python 3.7 [31] with panda [32], scipy [33], and matplotlib [34] packages.

3. Results and Discussion

As expected, our study revealed that the highest concentration of magnetic pollutants came from the PG site. This site is in the center of Wrocław and is one of the most traffic-heavy districts in the city, containing a major public transport artery. Samples collected from the indoor environment revealed higher mean values of χ compared with outdoor samples, whereas samples collected from spider webs exhibited higher mean values of χ compared with dust samples (159×10^{-8} $m^3 \cdot kg^{-1}$ for ID and 199×10^{-8} $m^3 \cdot kg^{-1}$ for ISW vs. 125×10^{-8} $m^3 \cdot kg^{-1}$ for OD and 159×10^{-8} $m^3 \cdot kg^{-1}$ for OSW) (Figure 2 and Table 2).

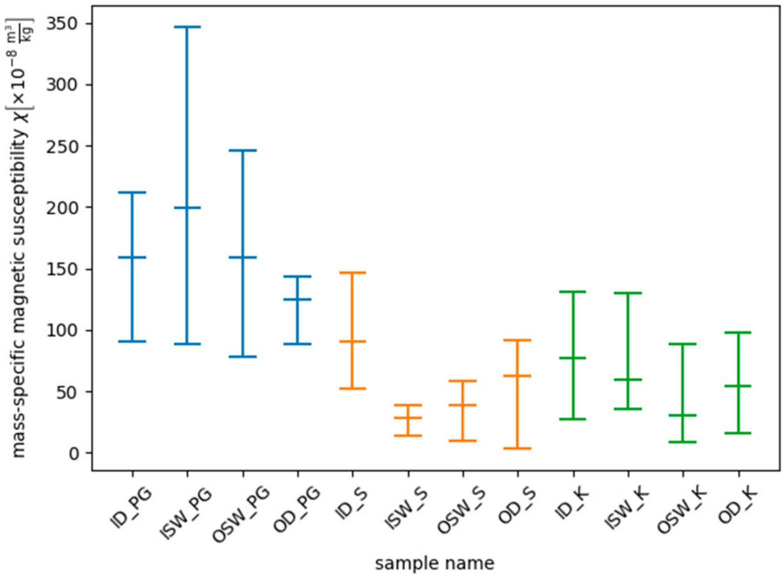

Figure 2. Mass-specific susceptibility values for samples (ID—indoor dust; ISW—indoor spider web; OSW—outdoor spider web; OD—outdoor dust) collected at different sites (PG—Grunwaldzki Square; S—Siemiradzkiego; K—Kamieńskiego). The whiskers range from minimum to maximum values, and the horizontal bars represent mean values.

Table 2. Comparison of indoor and outdoor χ ratios for spider webs (ISW/OSW) and dust samples (ID/OD) collected at different sites (PG—Grunwaldzki Square; S—Siemiradzkiego; K—Kamieńskiego).

	ISW/OSW	ID/OD
PG	$1.25^{+0.93}_{-0.54}$	$1.27^{+0.38}_{-0.31}$
S	$0.71^{+0.44}_{-0.26}$	$1.46^{+1.21}_{-0.61}$
K	$2.00^{+6.05}_{-1.26}$	$1.42^{+1.67}_{-0.73}$

The results obtained from spider webs can be compared with those presented in the research conducted by Rachwał et al. [23]. The study reported lower mean χ values for spider web samples collected in urban areas in Poland (χ = 52 × 10^{-8} $m^3 \cdot kg^{-1}$ for outdoor sites and χ = 29 × 10^{-8} $m^3 \cdot kg^{-1}$ for indoor sites); however, the individual results (indoor) were also around 100 × 10^{-8} $m^3 \cdot kg^{-1}$, most often due to the existence of an open fireplace in the room that was regularly used, not only in winter [23]. Magnetic susceptibility is a parameter that depends not only on the grain size of magnetic particles, but also on their mineralogy and elemental concentration; therefore, by comparing different data, the source and kind of pollution, season, weather conditions, and another site-specific factors can be taken into account. Studies that employed other magnetic biomonitors also recorded elevated χ values for outdoor areas with high vehicular traffic and industrial activity (e.g., up to 373 × 10^{-8} $m^3 \cdot kg^{-1}$ in Aburrá Valley, Colombia using epiphytic plant *Tillandsia* sp. [35], or up to 1161 × 10^{-8} $m^3 \cdot kg^{-1}$ using native lichen *Parmotrema pilosum* in Tandil city, Argentina) [36]. Furthermore, our results are comparable with other studies of the magnetic properties of outdoor road dust, e.g., Tao et al. [36] (mass-specific magnetic susceptibility of 109–163 × 10^{-8} $m^3 \cdot kg^{-1}$ for the East Lake area in Wuhan, China). Additionally, our results for the mean mass-specific magnetic susceptibility for indoor samples are in line with Szczepaniak-Wnuk and Górka-Kostrubiec [37], who investigated indoor dust collected using vacuum cleaners with bags from 20 apartments in Żyrardów, Poland (χ: 44–120 × 10^{-8} $m^3 \cdot kg^{-1}$ for the suburban area; 85–1000 × 10^{-8} $m^3 \cdot kg^{-1}$ for the city center area; average χ value for Żyradów: 116 × 10^{-8} $m^3 \cdot kg^{-1}$).

The mean mass-specific magnetic susceptibility values for outdoor spider webs at sites S and K were notably lower. For these sites, the vehicle traffic is significantly lower compared with that at PG, especially for site S, which is considered to be in a quiet part of Wrocław. In general, the mean mass-specific magnetic susceptibility values for K and S obtained from outdoor spider webs were in line with data for other residential sides obtained using different magnetic bioindicators, e.g., *Tillandsia* sp. (27×10^{-8} $m^3 \cdot kg^{-1}$) [35].

For samples collected at site S, the highest mean value for magnetic susceptibility was observed for indoor dust (ID = 91×10^{-8} $m^3 \cdot kg^{-1}$). By comparison, the χ value for indoor spider webs was nearly three-fold lower (ISW = 28×10^{-8} $m^3 \cdot kg^{-1}$) (Figure 2). As seen from this low χ value for ISW, site S was the only location where the magnetic susceptibility was lower for indoor samples than outdoor specimens (ISW/OSW χ ratio: $0.71^{+0.44}_{-0.26}$) (Table 2). For indoor dust samples, the mean magnetic susceptibility value was higher than that for outdoor samples (χ = 91×10^{-8} m^3 kg^{-1} for ID and χ = 62×10^{-8} $m^3 \cdot kg^{-1}$ for OD) (Figure 2 and Table 2).

Additionally, at site K, the samples collected indoors showed higher χ values compared with outdoor specimens (χ = 60×10^{-8} $m^3 \cdot kg^{-1}$ for ISW, χ = $77 \times 10^{--8}$ $m^3 \cdot kg^{-1}$ for ID vs. χ = 30×10^{-8} $m^3 \cdot kg^{-1}$ for OSW, χ = 54×10^{-8} $m^3 \cdot kg^{-1}$ for OD). It is interesting that in the prosthetic laboratory, where dentures, implants, and braces are prepared (among other items), for samples collected by spider webs, the indoor/outdoor χ ratio was the highest in the study (ISW/OSW χ ratio $2.00^{+6.05}_{-1.26}$: vs. $1.42^{+1.67}_{-0.73}$ for ID/OD χ ratio) (Table 2). Because many metallic elements are used in dental alloys (e.g., oxides of Au, Pd, Pt, Ir, Ru, Rh, Ag, Cu, and Ti), heightened levels of magnetic particulate pollution can be expected inside the laboratory [38]. Moreover, spider silk captures particles resulting from prosthetic processes (drilling, polishing, molding, etc.) regardless of their size, whereas the mass-specific magnetic susceptibility depends upon the precise particulate size, distribution, and morphology present within a sample. Spider silk may exhibit efficiency advantages over filter materials, because magnetic studies suggest that webs of some spider species can act as active filters for magnetic particles due to electrically conductive glue spreading across their surfaces [39,40].

The indoor/outdoor (I/O) ratio has been widely used to evaluate differences between indoor and outdoor pollutant concentrations. This ratio is useful for giving an indication of the strength of indoor pollutant sources. In this study, matching the I/O of the magnetic susceptibility for spider webs and dust samples allowed for a comparison of these matrices. It is notable that both approaches resulted in similar qualitative data (Table 2). Both methods (with the exception of spider webs at the S site) indicated heightened levels of magnetic pollutants in the indoor environment, with differences between the methods ranging between 2 and 50%.

Jordanova et al. [1] conducted a comprehensive magnetic study of I/O road dust from six cities in Bulgaria. For dust collected by brushing an initially clean surface, the mean indoor susceptibility values were lower than the corresponding outdoor values, whereas the susceptibility values of outdoor dust samples were half those of road dust (dust collected directly from roads next to outdoor sites). We observed the opposite ratio for I/O dust collected at corresponding sites, both from spider webs and filters. It must be considered that many factors affect indoor air quality and that the composition of indoor settled dust is influenced by outdoor contaminants. Furthermore, there are many distinct differences between these two types of sample [41–43]. Outdoor pollutants can infiltrate indoor areas due to diffusion and turbulent flow through natural and mechanical ventilation. The pollution level depends on the rate of pollutant transport from outdoors to indoors and the type of pollution source [44,45]. Various authors have proven that PM concentration levels depend on factors such as housing characteristics, PM sources, building and furnishing materials, and inhabitants' activities, e.g., cooking, heating, smoking tobacco, burning of candles, or grilling [46–48]. Yaghi et al. [49] studied concentrations of Pb, Cu, Ni, Zn, and Cr in outdoor and indoor dust samples collected from different sites in Muscat, Oman. The I/O ratios for mean concentrations revealed internally generated contamination of Pb, Zn, and Cu (I/O = 1.7, 5.7, 2.2, respectively). A study by Di Gilio et al. [50] showed higher concentrations of Ni and As in indoor dust samples compared with outdoor samples (I/O ratios of 2.5 and 1.4, respectively) in a primary school located in the south of Italy.

The prosthetic laboratory at site K is a potential source of various metallic particles with different granulations derived from technical procedures performed on prosthetic accessories (drilling, polishing, molding). Although both sampling methods revealed heightened levels of indoor-originated ferromagnetic particles, the spider web technique, in particular, highlighted this. Similarly, at the PG site, higher magnetic susceptibility values can be expected for samples collected in the environmental science laboratory compared with the outdoor environment. In the laboratory, there are various potential sources of metallic particles, such as gas burners that are frequently used by students (Teclu burners), dry heat sterilizers, or even ink printers [49]. In contrast, at site S, the mean mass-specific magnetic susceptibility value for samples collected by spider web indoors (in a room in a tenement house with no obvious magnetic particle sources) was considerably lower than that for samples collected outdoors. At this site, the opposite relationship was observed for dust sampling. However, it must be considered that for dust specimens, two sampling techniques were used for this study—passive (freefall indoor dust collected on filters) and active (outdoor road dust collected with a portable vacuum cleaner fitted with filter bags). Road dust consists primarily of soil-derived minerals (60%), with quartz averaging 40–50%, and various clay-forming minerals [50]. Vacuuming these diamagnetic components of road dust may dilute the signal from the technogenic magnetic pollutants. Thus, the mass-specific magnetic susceptibility of road dust samples may result in a lower mean χ value compared with that of dust collected indoors by passive exposition. In this case, a more reliable technique for comparing I/O magnetic particle pollution would involve deposition on spider webs due to the consistency of this sampling method.

The null hypothesis that samples are normally distributed has to be rejected for the samples collected from indoor spider webs (ISW) and for outdoor spider webs (OSW) at the Kamieńskiego site (K) (see Supplementary Materials; Table S1). The results of Welch's t-test are presented in the Supplementary Materials (Supplementary Table S2). The general result was that magnetic susceptibility values were not significantly different between samples ($\alpha = 0.05$). Firstly, we checked whether samples collected using different methods at a given site (outdoor and indoor spider webs, URD, and indoor settled dust on filters) were similar. The results (Supplementary Table S3) show that, in all cases, we cannot reject the null hypothesis that samples are similar ($p < 0.05$), whereas for only two pairs at the Siemiradzkiego (S) site and three pairs at the Kamieńskiego (K) site, we have to reject the null hypothesis ($p < 0.1$). A comparison of the given sample types between sites showed that the Grunwaldzki Square (PG) differs from other sites (Supplementary Table S4). The susceptibility of the collected indoor settled dust samples at site PG differed from other sites at $p < 0.1$, and the outdoor dust (OD) samples also differed at $p < 0.05$.

4. Conclusions

The aim of this study was to report the magnetic susceptibility of urban road dust settled indoors and outdoors, and to compare the results with data gathered using the spider web sampling method. Our study revealed elevated levels of anthropogenic ferromagnetic particle fractions (expressed by magnetic susceptibility values) in three sites in the city of Wrocław. The increase in the magnetic particle concentration in the area with heavy traffic load indicates that the main source of outdoor air pollution was vehicle emissions. However, the I/O ratio of the mean mass-specific magnetic susceptibility suggested the presence of indoor pollution sources in two of the investigated sites. The extent of the indoor ferromagnetic particle concentration depended on the impact of outdoor pollutants, building characteristics, room locations, specific internal sources, and users' habits. The indoor/outdoor ratios of magnetic susceptibility for the investigated matrices were highly comparable, although this ratio does not invalidate the use of spiders' webs as natural substrates for determining the provenance and nature of aeolian particulates in urban environments. However, when comparing the magnetic susceptibility results obtained for different matrices, care should be taken because the χ values depend on many factors, e.g., the particulate size, and because different matrices have the ability to trap particles with varied granulation and morphological characteristics.

Spider silk can provide data that is comparable not only to other biomonitors but also to classical methods. In comparison to conventional samplers, spider webs are practically costless, do not require any surveillance, and allow for long-time monitoring for weeks or even months. However, the higher coefficient variation of the mean mass-specific magnetic susceptibility of spider web samples compared to road dust collected on filters implies a need for better method standardization under laboratory conditions to obtain representative qualitative results for the local environment. This method may be used as a complement to traditional monitoring stations and could be a valuable addition to existing monitoring networks. In particular, in the case of indoor environments, spider silk can serve as a common, easily obtainable, efficient material for magnetic monitoring.

Supplementary Materials: The following are available online at http://www.mdpi.com/2075-163X/10/11/1018/s1, Table S1. Results of the Shapiro-Wilk test. Samples that are not normally distributed are marked green (significance $p < 0.01$). Table S2. The p value of Welch's t-test between samples at Grunwaldzki Square (PG) site, Siemiradzkiego (S) site and Kamieńskiego (K) site. If the hypothesis about equality of means can be rejected at $p < 0.1$ value is marked with orange. Table S3. The p value of Welch's t-test between samples collected at indoor dust filters (ID), indoor spider webs (ISW), outdoor dust filters (OD), outdoor spider webs (OSW). If the hypothesis about equality of means can be rejected at $p < 0.1$ value is marked with orange, for $p < 0.05$ value is marked with yellow, for $p <$ 0.01. Table S4. Pearson correlation matrix on metal concentrations at all sites. Statistically significant correlations: $p < 0.01$ green, $p < 0.05$ yellow, $p < 0.1$ orange.

Author Contributions: Conceptualization, R.R. and J.R.; formal analysis, R.R. and J.S.B.; investigation, M.R.; resources, R.R., J.S.B., M.R., W.R.-K. and J.R.; supervision, W.R.-K. and J.R.; writing—original draft, R.R.; writing—review and editing, M.R. All authors have read and agreed to the published version of the manuscript.

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

References

1. Jordanova, D.; Jordanova, N.; Lanos, P.; Petrov, P.; Tsacheva, T. Magnetism of outdoor and indoor settled dust and its utilization as a tool for revealing the effect of elevated particulate air pollution on cardiovascular mortality. *Geochem. Geophys. Geosyst.* **2012**, *13*, 8. [CrossRef]
2. Donaldson, K.; Tran, L.; Jimenez, L.A.; Duffin, R.; Newby, D.E.; Mills, N.L.; MacNee, W.; Stone, V. Combustion-derived nanoparticles: A review of their toxicology following inhalation exposure. *Part. Fibre Toxicol.* **2005**, *2*, 10. [CrossRef] [PubMed]
3. Mitchell, R.; Maher, B.A. Evaluation and application of biomagnetic monitoring of traffic-derived particulate pollution. *Atmos. Environ.* **2009**, *43*, 2095–2103. [CrossRef]
4. Kim, W.; Doh, S.-J.; Park, Y.-H.; Yun, S.-T. Two-year magnetic monitoring in conjunction with geochemical and electron microscopic data of roadside dust in Seoul, Korea. *Atmos. Environ.* **2007**, *41*, 7627–7641. [CrossRef]
5. Muxworthy, A.R.; Matzka, J.; Petersen, N. Comparison of magnetic parameters of urban atmospheric particulate matter with pollution and meteorological data. *Atmos. Environ.* **2001**, *35*, 4379–4386. [CrossRef]
6. Muxworthy, A.R.; Matzka, J.; Davila, A.F.; Petersen, N. Magnetic signature of daily 1595 sampled urban atmospheric particles. *Atmos. Environ.* **2003**, *37*, 4163–4169. [CrossRef]
7. Gómez-Paccard, M.; McIntosh, G.; Villasante-Marcos, V.; Lopez, M.L.O.; Rodríguez-Fernández, J.; Gomez-Sal, J. Low-temperature and high magnetic field measurements of atmospheric particulate matter. *J. Magn. Magn. Mater.* **2004**, *272*, 2420–2421. [CrossRef]
8. Szczepaniak-Wnuk, I.; Górka-Kostrubiec, B. Magnetic particles in indoor dust as marker of pollution emitted by different outside sources. *Stud. Geophys. Geod.* **2016**, *60*, 297–315. [CrossRef]
9. Sagnotti, L.; Taddeucci, J.; Winkler, A.; Cavallo, A. Compositional, morphological, and hysteresis characterization of magnetic airborne particulate matter in Rome, Italy. *Geochem. Geophys. Geosyst.* **2009**, *10*, 8. [CrossRef]

10. Jeleńska, M.; Górka-Kostrubiec, B.; Werner, T.; Kądziałko-Hofmokl, M.; Szczepaniak-Wnuk, I.; Gonet, T.; Szwarczewski, P. Evaluation of indoor/outdoor urban air pollution by magnetic, chemical and microscopic studies. *Atmos. Pollut. Res.* **2017**, *8*, 754–766. [CrossRef]
11. Wan, D.; Han, Z.; Yang, J.; Yang, G.; Liu, X. Heavy metal pollution in settled dust associated with different urban functional areas in a heavily air-polluted city in North China. *Int. J. Environ. Res. Public Health* **2016**, *13*, 1119. [CrossRef] [PubMed]
12. Márton, E.; Zajzon, N.; Lautner, P.; Sipos, P.; Szentmarjay, T.; Pethe, M. Magnetic monitoring, geochemical and mineralogical analysis of settled dust from North and Central Transdanubia, Hungary. *Central Eur. Geol.* **2012**, *55*, 347–364. [CrossRef]
13. Zajzon, N.; Márton Péterné Szalay, E.; Sipos, P.; Pethe, M.; Németh, T.; Kovácsné Kis, V. Tracking magnetic pollutants by integrated mineralogical and magnetic analyses of airborne particles in urban environment. *Carpathian J. Earth Environ. Sci.* **2013**, *8*, 221–229.
14. Cao, L.; Appel, E.; Hu, S.; Ma, M. An economic passive sampling method to detect particulate pollutants using magnetic measurements. *Environ. Pollut.* **2015**, *205*, 97–102. [CrossRef]
15. Hofman, J.; Maher, B.A.; Muxworthy, A.R.; Wuyts, K.; Castanheiro, A.; Samson, R. Biomagnetic monitoring of atmospheric pollution: A review of magnetic signatures from biological sensors. *Environ. Sci. Technol.* **2017**, *51*, 6648–6664. [CrossRef]
16. Salo, H.; Bućko, M.S.; Vaahtovuo, E.; Limo, J.; Mäkinen, J.; Pesonen, L.J. Biomonitoring of air pollution in SW Finland by magnetic and chemical measurements of moss bags and lichens. *J. Geochem. Explor.* **2012**, *115*, 69–81. [CrossRef]
17. Kodnik, D.; Winkler, A.; Carniel, F.C.; Tretiach, M. Biomagnetic monitoring and element content of lichen transplants in a mixed land use area of NE Italy. *Sci. Total Environ.* **2017**, *595*, 858–867. [CrossRef]
18. Flanders, P.J. Collection, measurement, and analysis of airborne magnetic particulates from pollution in the environment (invited). *J. Appl. Phys.* **1994**, *75*, 5931–5936. [CrossRef]
19. Hose, G.C.; James, J.; Gray, M. Spider webs as environmental indicators. *Environ. Pollut.* **2002**, *120*, 725–733. [CrossRef]
20. Xiao-Li, S.; Yu, P.; Hose, G.; Jian, C.; Feng-Xiang, L. Spider webs as indicators of heavy metal pollution in air. *Bull. Environ. Contam. Toxicol.* **2006**, *76*, 271–277. [CrossRef]
21. 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] [PubMed]
22. Rybak, J. Accumulation of major and trace elements in spider webs. *Water Air Soil Pollut.* **2015**, *226*, 1–12. [CrossRef] [PubMed]
23. Rachwał, M.; Rybak, J.; Rogula-Kozłowska, W. Magnetic susceptibility of spider webs as a proxy of airborne metal pollution. *Environ. Pollut.* **2018**, *234*, 543–551. [CrossRef] [PubMed]
24. Foelix, R.F. *Biology of Spiders*; Oxford University Press: Oxford, UK, 2011; Volume 14.
25. Roberts, M.J. *Spiders of Britain and Northern Europe*; Harper Collins: London, UK, 1995.
26. 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]
27. Shapiro, S.S.; Wilk, M.B. An analysis of variance test for normality (Complete Samples). *Biometrika* **1965**, *52*, 591. [CrossRef]
28. Welch, B.L. The Generalization of 'Student's' Problem when Several Different Population Variances are Involved. *Biometrika* **1947**, *34*, 28. [CrossRef]
29. Wilcoxon, F. Individual comparisons by ranking methods. *Biom. Bull.* **1945**, *1*, 80. [CrossRef]
30. Wasserman, L. All of Statistics: A Concise Course in Statistical Inference Brief Contents. *Simulation* **2004**. [CrossRef]
31. Python Software Fundation. *Python Language Reference*; Version 3.7; Python Software Foundation: Beaverton, OR, USA, 2020.
32. McKinney, W. Data Structures for Statistical Computing in Python. In Proceedings of the 9th Python in Science Conference, Austin, TX, USA, 28 June–3 July 2010.
33. Virtanen, P.; Gommers, R.; Oliphant, T.E.; Haberland, M.; Reddy, T.; Cournapeau, D.; Burovski, E.; Peterson, P.; Weckesser, W.; Bright, J.; et al. SciPy 1.0: Fundamental algorithms for scientific computing in Python. *Nat. Methods* **2020**, *17*, 261–272. [CrossRef]

34. Hunter, J.D. Matplotlib: A 2D Graphics Environment. *Comput. Sci. Eng.* **2007**, *9*, 90–95. [CrossRef]
35. Mejía-Echeverry, D.; Chaparro, M.A.E.; Trujillo, J.D.; Miranda, A.G.C.; Chaparro, M.A.E. Magnetic Biomonitoring as a Tool for Assessment of Air Pollution Patterns in a Tropical Valley Using Tillandsia sp. *Atmosphere* **2018**, *9*, 283. [CrossRef]
36. Marié, D.C.; Chaparro, M.A.E.; Irurzun, M.A.; Lavornia, J.M.; Marinelli, C.; Cepeda, R.; Böhnel, H.N.; Miranda, A.G.C.; Sinito, A.M. Magnetic mapping of air pollution in Tandil city (Argentina) using the lichen Parmotrema pilosum as biomonitor. *Atmos. Pollut. Res.* **2016**, *7*, 513–520. [CrossRef]
37. Górka-Kostrubiec, B.; Jelenska, M.; Król, E. Magnetic signature of indoor air pollution: Household dust study. *Acta Geophys.* **2014**, *62*, 1478–1503. [CrossRef]
38. Malara, P.; Fischer, A.; Malara, B. Selected toxic and essential heavy metals in impacted teeth and the surrounding mandibular bones of people exposed to heavy metals in the environment. *J. Occup. Med. Toxicol.* **2016**, *11*, 1–11. [CrossRef] [PubMed]
39. Vollrath, F.; Edmonds, D. Consequences of electrical conductivity in an orb spider's capture web. *Naturwissenschaften* **2013**, *100*, 1163–1169. [CrossRef] [PubMed]
40. Samu, F.; Matthews, G.A.; Lake, D.; Vollrath, F. Spider webs are efficient collectors of agrochemical spray. *Pestic. Sci.* **1992**, *36*, 47–51. [CrossRef]
41. Culbard, E.; Thornton, I.; Watt, J.; Wheatley, M.; Moorcroft, S.; Thompson, M. Metal Contamination in British Urban Dusts and Soils. *J. Environ. Qual.* **1988**, *17*, 226–234. [CrossRef]
42. Rasmussen, P.; Subramanian, K.; Jessiman, B. A multi-element profile of house dust in relation to exterior dust and soils in the city of Ottawa, Canada. *Sci. Total Environ.* **2001**, *267*, 125–140. [CrossRef]
43. Arar, S.; Al-Hunaiti, A.; Masad, M.; Maragkidou, A.; Wraith, D.; Hussein, T. Elemental Contamination in Indoor Floor Dust and Its Correlation with PAHs, Fungi, and Gram+/− Bacteria. *Int. J. Environ. Res. Public Health* **2019**, *16*, 3552. [CrossRef]
44. Kulmala, M.; Asmi, A.; Pirjola, L. Indoor air aerosol model: The effect of outdoor air, filtration and ventilation on indoor concentrations. *Atmos. Environ.* **1999**, *33*, 2133–2144. [CrossRef]
45. Weschler, C.J.; Shields, H. The effects of ventilation, filtration, and outdoor air on the composition of indoor air at a telephone office building. *Environ. Int.* **1989**, *15*, 593–604. [CrossRef]
46. Castro, D.; Slezakova, K.; Delerue-Matos, C.; Alvim-Ferraz, M.C.; Morais, S.; Pereira, M.C. Contribution of traffic and tobacco smoke in the distribution of polycyclic aromatic hydrocarbons on outdoor and indoor PM2.5. *Glob. Nest J.* **2010**, *12*, 3–11.
47. 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]
48. Rutkowski, R.; Rybak, J.; Rogula-Kozłowska, W.; Bełcik, M.; Piekarska, K.; Jureczko, I. Mutagenicity of indoor air pollutants adsorbed on spider webs. *Ecotoxicol. Environ. Saf.* **2019**, *171*, 549–557. [CrossRef] [PubMed]
49. Xue, M.; Wang, S.; Huang, C. Determination of heavy metals (Pb,Cd,Cr and Hg) in printed paper as food packaging materials and analysis of their sources. *CIESC J.* **2010**, *12*, 32.
50. Gunawardana, C.; Goonetilleke, A.; Egodawatta, P.; Dawes, L.A.; Kokot, S. Source characterisation of road dust based on chemical and mineralogical composition. *Chemosphere* **2012**, *87*, 163–170. [CrossRef]

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