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Health risk assessment in the vicinity of a copper smelter: particulate matter collected on a spider web

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Abstract

We used spider webs as a particulate matter (PM) sampler to assess the possible health risk to the inhabitants of Legnica city (Poland). We aimed to find out if it is a useful material and could provide reliable information. We selected two spider families (Agelenidae and Linyphiidae) whose webs structure enhances the PM accumulation. The collected particles were analysed using a Scanning Electron Microscope equipped with Energy Dispersive X-Ray (SEM-EDX) and Inductively Coupled Plasma Mass Spectrometry (ICP-MS) which provided morphological and chemical information and allowed to indicate possible sources of pollution. The results showed that PM_{10}, the fraction of particles smaller than 10 μm, was dominated by the particles of natural origin, while fine fractions were composed of diverse anthropogenic particles, whose origin can be connected with the activity of the copper smelter and in smaller quantity with the road traffic. The carcinogenic and non-carcinogenic health risk was assessed for these pathways: inhalation, ingestion, and dermal, for children and adults. The non-carcinogenic risk was very high (Hazard Index: HI > 1) both for children (Cu, Ni, Pb, Cd) and adults (Cu, As, Pb, Cd). Moreover, high carcinogenic risk ($>10^{-4}$) was found in most of the sampling points. The study shows that spider webs are useful in biomonitoring of PM and can also be used for health risk assessment. In the studied region, it was found that the possible negative impact of air pollution on human health exists.

Keywords: air pollution, spider web, PM, Scanning Electron Microscopy, health hazard

1. Introduction

Biomonitoring is a method where living organisms, their parts, or even their products are used to quantitatively assess the quality of the environment (Markert 2007). In air pollution assessment, mosses (Kosior et al. 2008; Kosior et al. 2015; Schintu et al. 2005), lichens (Ciężka et al. 2018; Massimi et al. 2019; Stojanowska et al. 2020), tree leaves and needles (Górka et al. 2020; Stojanowska et al. 2021; Teper 2009; Wang et al. 2015) are well-known and frequently used. One of the newest tools used in biomonitoring is the application of spider web. Increasingly, it has become the subject of research by scientists due to its unique properties and the fact that it is easily accessible, cheap, and can provide sufficient information about air pollution (Bartz et al. 2021; Górka et al. 2018; Stojanowska et al. 2022). In previous studies, spider web has been mostly used to discriminate particulate matter (PM) collected on its threads (Bartz et al. 2021; Górka et al. 2018; Hose et al. 2002; Rybak 2015; Stojanowska et al. 2021; Xiao-li et al. 2006).

However, many of such studies treat only the chemical composition of the collected PM, while the most important is the form and the fraction in which given metals are present and their possible impact on human health. The studies where the health risk has been assessed are numerous, although they are mainly based on airborne dust samples (total suspended particles (TSP) and particles smaller than 2.5 µm ($PM_{2.5}$)) collected on different filters (e.g. Behrooz et al. 2021).

Nowadays, when air pollution is a growing concern, alternative methods are searched in order to make the air pollution assessment cheaper, easier and eco-friendly. All of these advantages are represented by spider webs. Moreover, there is a possibility of breeding spiders in the laboratory and transplanting the webs woven by them to any place to assess the level of contamination and ease determination of the exposure time (Rybak, Olejniczak 2014; Stojanowska et al. 2020). Previous studies have shown that the web obtained from laboratory breeding has negligible amounts of elements (Górka et al. 2018) different time of spider web exposure was tested as a factor influenced final quality and quantity interpretation of data. Samples were collected from three sites in Wrocław city (SW Poland, so it can be treated as an uncontaminated sample.

With this unique material, we assessed the differentiation of PM collected on threads, its form, size, and the exact amount of potentially toxic elements (PTEs). Scanning Electron Microscope equipped with Energy Dispersive X-Ray (SEM-EDX) analysis of pollution accumulated on spider webs provided mineralogical composition, shape, and size of particles. Web analysis using Inductively Coupled Plasma Mass Spectrometry (ICP-MS) gave quantitative information about the precise amount of PTEs collected on threads. Based on this data, the health hazard for people living in Legnica city was assessed. This city is located in southwestern Poland and is known for its copper smelter industry. What is more, there are many commonly used roads nearby, known for high traffic. The pollution originating from the transport can derive from exhaust traffic related particles or non-exhaust traffic related particles. The first group is emitted from incomplete fuel combustion. On the other hand, the second one can especially originate from tire, brakes, and clutch abrasion or road surface but also from the resuspension of already existing particles from the road due to car traffic (Grigoratos, Martini 2014). Brake wear particles are characterized by the presence of Fe, Cu, Zn, Sn, Sb and S, while in tire wear particles, high amounts of Zn, Cu and S can be noted (Grigoratos, Martini 2014). Vehicle exhaust should still be considered one of the sources of Pb pollution (Hong et al. 2018).

In this study, two different methods, SEM-EDX and ICP-MS, were combined, which allowed us to assess the impact of the smelter. Finally, the complex assessment of possible health hazards in this region connected with the presence of PTEs in the air was performed. Based on these methods, it was shown that the impact of the Legnica copper smelter is notable and what is more that carcinogenic and non-carcinogenic risks exist in this area. To the authors' best knowledge, studies of health risk assessment based on PM collected on spider webs have never been conducted before.

2. Samples and methods

2.1. Study area

The study was carried out in Legnica city, located in southwestern Poland (Lower Silesia voivodship). Close to this city is a center of copper mining and processing (KGHM - Copper Mining and Metallurgical Combine). The company is considered the first largest silver producer and the sixth producer of electrolytic copper in the world. Currently, the Legnica smelter produces over 120,000 tons of copper cathodes (99.99% Cu) annually. The copper cathodes are the final product but additionally, the sludge remaining after electrorefining is the starting material for producing silver, gold, and platinum concentrate. As a result of conducted technological process in the individual parts of installations, sulfuric acid, copper sulfate, nickel sulfate, and refined lead are also produced (KGHM 2022). The production in this smelter is based on the technology of smelting copper concentrates in shaft furnaces, and technical gases produced in these furnaces are transferred after dedusting to the heat and power plant, which uses them to produce energy. On the other hand, the dust from the dedusting (zinc concentrate, ~47% of Zn) is entirely used as a raw material for the production of zinc compounds. The other waste semi-products are slag from furnaces, used in the production of building aggregates, and sludges from wet gas dedusting and dust from converter gas dedusting (Pb-bearing concentrates, 30-50% Pb) are immediately used or partly stored for future use (Topolnicki 2021). In 2019, the Legnica copper smelter started the performance tests of a new anode furnace for producing copper anodes. The new furnace is said to be equipped with an efficient installation for the purification of process gases (KGHM 2022). Next, in 2021 a technological node was built to remove arsenic and mercury from the Solinox installation, which is responsible for the purification of gases generated in the copper production process (Topolnicki 2021). Even though the emission of fly ash material, containing large amounts of heavy metals, was significantly reduced compared to the 1980s and 1990s, the company is still considered to have a negative effect on the local environment (Kostecki et al. 2015; Stojanowska et al. 2020; Strzelec, Niedźwiecka 2012; Tyszka et al. 2016). The study area of Legnica is crossed by commonly used roads: express national road S3, with about 18 000 motor vehicles per day, and national road 94, with over 7 000 cars daily. There is also an A4 highway, situated southward from the city, and characterized by about 30 000 motor vehicles per day (GDDKiA 2015). As claimed in Information On Air Quality In The Area Of Legnica City, transport input in the production of PM_{10} and $PM_{2.5}$ is 24% and 13%, respectively (Mikołajczyk et al. 2017). Moreover, there are also two heat and power stations: one located in Wrocław, 60 km away from Legnica, and the other (Czechnica), situated about 70 km from Legnica. Apart from that, there is a power station Turów, about 90 km from Legnica (Fig. 1).

2.2. Environmental parameters

During this study (mid-June to mid-September 2018), the maximal temperature in Legnica reached 32°C (during the day) while the minimum temperature was 6°C (during the night) (Weather Online 2018). The climate in this area can be classified as temperate continental and is considered relatively humid. The dominant wind direction in the studied area is west, with smaller addition of winds from south and southwest (Dancewicz et al. 2009).

Air quality in Lower Silesia Voivodeship in 2018 was admissible. However, in the Legnica Regional Inspectorate of Environmental Protection (RIEP) monitoring station, the concentration of PM_{10}, higher than the limit (50 µg/m^3), was noted for 65 days, while the limit with observed exceedings according to air quality directive (2008/EC/50) by European Union is 35 days per year. For the $PM_{2.5,}$ the exceeding of the average annual norm was not observed, but the level of $PM_{2.5}$ in Legnica reached the maximum level equal to 25 µg/m^3. The concentrations of Cd, Ni, and Pb in the PM_{10} did not exceed the permissible levels in the studied area, while for As, the average annual level in the PM_{10} was exceeded, reaching 8.30 ng/m^3. Those results were recorded in Rzeczypospolitej street in Legnica (located ~4 km northeastward from our study area) (GIOŚ 2019).

2.3. Spiders characteristic

During the previous studies, it has been proven that the webs of Agelenidae and Linyphiidae families are the most suitable for the indication of pollutants since their webs are relatively compact and of high density facilitating the accumulation of pollutants in their surface (Bartz et al. 2021; Rybak and Olejniczak 2014). Therefore, the very common species *Eratigena atrica* (Agelenidae) and *Linyphia triangularis* (Linyphiidae) have been chosen for studies. Agelenids' webs are in the form of dry, not sticky sheet with signal threads attached (Roberts 1995; Rybak, Olejniczak, 2014). The family members usually live in the urban or industrial environment, and females are present all year round (Rybak, Olejniczak 2014), which facilitates sampling during wintertime. Similarly, Linyphiidae representatives weave large, not sticky webs in the form of a sheet (Roberts 1995). Linyphiids are suitable for studies, although they prefer natural elements of landscape, thus, they rarely occur near industries or other polluted areas.

2.4. Methods

2.4.1. Samples collection

The sampling of spider webs was conducted from mid-July to mid-September in 2018. Seven sites were chosen within the Legnica area (sampling points 2, 3, 4, 5, 10, 11, 13; Fig. 1). In a few cases, we applied the newly constructed webs only with a known number of exposure days from its creation to define the exposure time (we removed the old web). Therefore, the previously chosen sites have been visited and observed on a daily routine. Additionally, clean webs produced in the laboratory were used for transplantation. Webs derived from laboratory breeding of spiders were suspended on the frame of each Petri dish and exposed to pollutants at each site. The exposure time was three months for all webs at the same time. All webs were exposed at similar previously chosen sites near shrubs, bushes, low buildings, fences, or walls. Afterward, webs were introduced into the clean glass vials with sterile glass baguettes and transported to the laboratory.

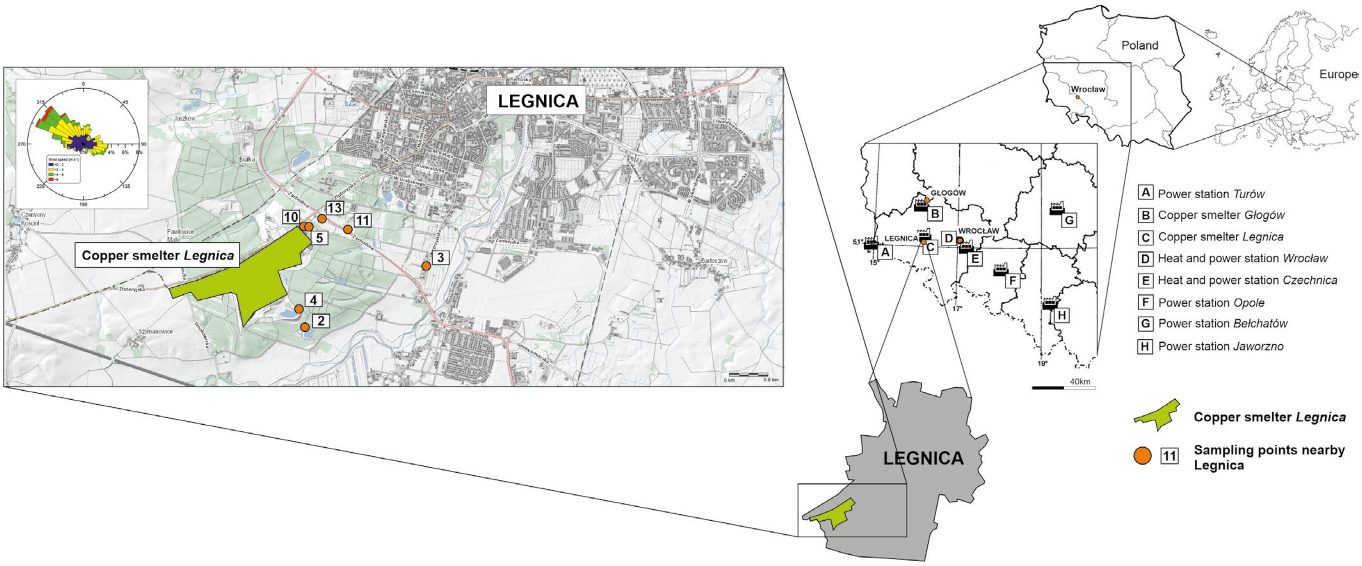

Figure 1. Location of sampling points 2-13 in the vicinity of smelter (Legnica) where spider webs belonging to Agelenidae and Linyphiidae families were taken. The source of the data is the Institute of Meteorology and Water Management - National Research Institute (IMGW-PIB). The data of the IMGW-PIB have been processed to create a wind graph. The source of the base map is Geoportal Dolny Śląsk (https://geoportal.dolnyslask.pl/imap/#gpmap=gp98).

2.4.2. SEM-EDX analyses

PM deposited on threads of spider webs was analysed with the use of SEM-EDX in order to determine its chemical composition. At the beginning, samples were carefully transferred to a glass slide covered with double-sided sticky carbon strips. Particular attention was given not to tangle the web, which would falsify the results. Then, each sample was coated with carbon to achieve ~30 nm thick layer with the Cressington 108C Auto Carbon Coater equipped with an MTM-10 High Resolution Thickness Monitor. Samples prepared in such a way were then subjected to analysis using a Jeol JSM IT-100 scanning microscope (JEOL, Akishima City, Tokyo, Japan) with Oxford EDX system in the mode of secondary electrons (SE) and backscattered electrons (BSE). SEM was operated at high-vacuum mode and acceleration voltage equal to 14 kV. At first, the samples were analysed at low magnification in order to check the spatial distribution of collected PM. After this, random spots of representative areas were selected, and for each sample, a set of microphotographs at different magnifications were taken (magnification: 100×, 500x, 1000×, and 2000×). In total, approximately 1 mm^2 of each sample was analysed. EDX microanalysis was conducted with 120 s of capture time with 50 to 100 counts/second and <20% dead time, which allowed EDX analysis at the central part of the particles to be recorded. The minimum detection limit of EDX analysis was equal to 0.2%.

Obtained EDX spectra were then compared with the previously presented data (Deer et al. 2013; Reed 2005). The purpose was to differentiate particles of anthropogenic origin from natural ones of geological background. Differences noted between the chemical composition of minerals and chemical analyses of selected particles resulted in considering the particle as anthropogenic. In the process of differentiating the particles, the geological structure of the surface formations (geogenic background) in the area of Legnica was taken into account.

Acquisition of SEM images allowed to determine the size distribution of PM on threads (based on the longest Feret diameter) which was conducted using JMicroVision software (Roduit 2007) and then led to the division of mineralogical phases into size-dependent groups. Finally, with the use of Grapher (Grapher™ from Golden Software, LLC, Golden, CO, USA, www.goldensoftware.com), the charts of mineralogical phases present in different fractions were prepared. Maps of the spatial distribution of atmospheric particles originating from anthropogenic activity were constructed with the use of Surfer (Surfer® from Golden Software, LLC, Golden, CO, USA, www.goldensoftware.com).

2.4.3. ICP-MS analyses

In order to determine the exact chemical composition of the particles collected on the spider web, ICP-MS analysis was performed. The analysis was conducted by the central laboratory of the Institute of Environmental Engineering Polish Academy of Sciences in Zabrze, using Elan 6100 DRC-e Perkin (Perkin Elmer, Waltham, MA, USA). All of the analyses were done in accordance with the PN-EN ISO/IEC 17025 norm. Concentrations of the following elements were analyzed: As, Cu, Cd, Ni, Pb, and Zn. At first, all of the web samples (~0.06 g each) were weighed, flooded with nitric acid (3 ml; Suparpur®, Sigma-Aldrich), and next heated for 6 hours in a temperature between 80 and 90°C. The solution was then filtrated using a 0.22-μm polyethersulfone membrane filter and analyzed in triplicates. The operating conditions were as follows: ICP radio frequency power: 1125 W; nebuliser gas flow rate: 0.78–0.83 L/min; auxiliary gas flow: 1.15 L/min; plasma gas flow: 15 L/min; and sample flow rate: 1 mL/min. Certified multi-element standard stock solutions of Periodic table mix 1 and Transition metal mix 2 (Fluka) were used for calibration solution, and certified reference materials (SRM 1643e and SRM 1648a) obtained from the National Institute of Standard and Technology (NIST), were used for validation of this method. These certified reference materials were treated the same way as the spider web samples. The detection limits were as shown here: 0.019 μg/L for As, 0.048 μg/L for Cu, 0.018 μg/L for Cd, 0.017 μg/L for Ni, 0.134 μg/L for Pb, and 0.151 μg/L for Zn.

2.4.4. Health risk assessment

2.4.4.1. Exposure dose

Health risk assessment for the inhabitants of the smelter area was done according to the US EPA recommendations (US EPA 2009). It was calculated for the following elements: Cu, Zn, Ni, As, Pb, Cd, and the exposure throughout the life of the average child and adult via the oral, inhalation, and dermal routes was assessed, from which we consider the inhalation route the most crucial. We calculated the average concentration of elements per day and 1 kg of body weight (US EPA 2014; US EPA 2001). The exposure dose was determined as follows:

$$ADD_{ing} = C \cdot \frac{IngR \cdot EF \cdot ED}{BW \cdot AT} \quad (1)$$

$$ADD_{inh} = C \cdot \frac{InhR \cdot EF \cdot ED}{PEF \cdot BW \cdot AT} \cdot 10^6 \quad (2)$$

$$ADD_{iderm} = C \cdot \frac{SL \cdot SA \cdot ABS \cdot EF \cdot ED}{BW \cdot AT} \quad (3)$$

where:
C - average element concentration in spider webs [mg/kg];
IngR - value of daily accidental dust intake [mg/d];
InhR - daily lung ventilation [m^3/d];
EF - contact frequency [d/year];
ED - duration of contact [year];
BW - average body weight [kg];
AT - averaging period [d];
PEF - particle emission factor [m^3/kg];
SL - coefficient of dust adherence to the skin [$mg/cm^2 \cdot d$];
SA - skin surface exposed to dust [cm^2];
ABS - percutaneous absorption coefficient, unknown quantity.

All defined above values are in accordance with US EPA (1989) and are shown in Supplementary Table S1.

2.4.4.2. Non-cancerogenic health risk assessment

Non-carcinogenic health risk hazard quotient (HQ) and hazard index (HI) were used to determine non-cancerogenic health risk and calculated according to the following formulas:

$$HQ = \frac{ADD}{RfD} \quad (4)$$

$$HI = \Sigma HQ \quad (5)$$

where:
ADD - ingestion, inhalation or dermal dose;
RfD - reference dose, given in the Integrated Information Risk System (IRIS) (Jain et al. 2017; US EPA 2004) (Supplementary Table S2).
HQ > 1 and HI > 1 signify adverse effects on human health, while for HQ < 1 and HI < 1, there is no health risk or health hazard (US EPA 1989).

2.4.4.3. The assessment of cancer risk

The excess cancer risk (ECR) is based only on inhalation exposure, and it is calculated for carcinogenic elements only (Ni, Cd, and As) according to the following formula (Olawoyin et al. 2018)

$$ECR = \frac{C \cdot ET \cdot EF \cdot ED \cdot IUR}{BW \cdot AT} \quad (6)$$

where:
ET - exposure time [h/d];
IUR – slope factor [$\mu g/m^3$];
Meanings of C, EF, ED, BW, AT are the same as above. The IUR values of Cd, Ni, and As are 0.0018, 0.00024, and 0.0043. The rest of the parameters are the same as for the calculation of HQ and HI. If ECR is within 10^{-6} – 10^{-4}, there is a low risk of cancer.

2.4.5. Statistical analyses

All of the calculations were performed with the use of Statistica 13.1 software (StataCorp. 2013). At first, the Shapiro–Wilk's W test was done in order to examine the normality of the data. Next, due to the lack of normality of a part of the data set, Spearman's correlation coefficients were calculated (Sokal, Rohlf 2012) to check the possible correlations between analyzed parameters.

Table 1. Ranges (minimum-maximum) of Average Daily Dose (ADD; mg/kg; where ADDing - Average Daily Dose for ingestion, ADDinh - Average Daily Dose for inhalation, ADDderm - Average Daily Dose for dermal route), Hazard Quotient (HQ) and Hazard Index (HI) for adults and children exposed via oral, inhalation, and dermal routes. HQ > 1 and HI > 1 are marked in bold.

		Cu	Zn	Ni	As	Pb	Cd
Adults							
	ADDing	$2.27\cdot10^{2}$- $1.65\cdot10^{5}$	$1.06\cdot10^{3}$- $9.04\cdot10^{4}$	$3.14\cdot10^{1}$- $8.19\cdot10^{3}$	$1.01\cdot10^{1}$- $1.15\cdot10^{4}$	$3.91\cdot10^{2}$- $8.84\cdot10^{4}$	$6.59\cdot10^{0}$- $7.39\cdot10^{2}$
	ADDinh	$1.63\cdot10^{-2}$- $1.18\cdot10^{-1}$	$3.06\cdot10^{-2}$- $6.5\cdot10^{0}$	$2.26\cdot10^{-3}$- $5.89\cdot10^{-1}$	$7.25\cdot10^{-4}$- $8.25\cdot10^{-1}$	$2.81\cdot10^{-2}$- $6.36\cdot10^{0}$	$4.74\cdot10^{-4}$- $5.31\cdot10^{-2}$
	ADDderm	$4.53\cdot10^{0}$- $3.29\cdot10^{3}$	$8.48\cdot10^{0}$- $4.21\cdot10^{1}$	$6.27\cdot10^{-1}$- $1.63\cdot10^{2}$	$2.01\cdot10^{-1}$- $2.29\cdot10^{2}$	$7.79\cdot10^{0}$- $1.76\cdot10^{3}$	$1.31\cdot10^{-1}$- $1.47\cdot10^{1}$
Children							
	ADDing	$5.29\cdot10^{2}$- $3.84\cdot10^{5}$	$9.91\cdot10^{2}$- $2.11\cdot10^{5}$	$7.33\cdot10^{1}$- $1.91\cdot10^{4}$	$2.35\cdot10^{1}$- $2.68\cdot10^{4}$	$9.11\cdot10^{2}$- $2.06\cdot10^{5}$	$1.54\cdot10^{1}$- $1.72\cdot10^{3}$
	ADDinh	$2\cdot10^{-2}$- $2.1\cdot10^{1}$	$5.42\cdot10^{-2}$- $1.15\cdot10^{1}$	$4.01\cdot10^{-3}$- $1.05\cdot10^{0}$	$1.29\cdot10^{-3}$- $1.46\cdot10^{0}$	$1\cdot27^{-1}$- $1.13\cdot10^{1}$	$8.51\cdot10^{-4}$- $9.42\cdot10^{-2}$
	ADDderm	$2.96\cdot10^{0}$- $2.15\cdot10^{3}$	$5.55\cdot10^{0}$- $7.4\cdot10^{1}$	$4.11\cdot10^{-1}$- $1.07\cdot10^{2}$	$1.32\cdot10^{-1}$- $1.5\cdot10^{2}$	$1.3\cdot10^{1}$- $1.15\cdot10^{3}$	$8.61\cdot10^{-2}$- $9.56\cdot10^{0}$
Adults							
	HQing	$5.67\cdot10^{-3}$- **$4.12\cdot10^{0}$**	$1.42\cdot10^{-3}$- $3.01\cdot10^{-1}$	$1.57\cdot10^{-3}$- $4.1\cdot10^{-1}$	$1.62\cdot10^{-1}$- **$3.82\cdot10^{1}$**	$1.55\cdot10^{-1}$- **$2.53\cdot10^{1}$**	$6.59\cdot10^{-3}$- $7.39\cdot10^{-1}$
	HQinh	$4.08\cdot10^{-7}$- $2.96\cdot10^{-4}$	$1.02\cdot10^{-7}$- $2.17\cdot10^{-5}$	$1.13\cdot10^{-7}$- $2.95\cdot10^{-5}$	-	$7.98\cdot10^{-6}$- $1.81\cdot10^{-3}$	$4.74\cdot10^{-7}$- $5.31\cdot10^{-5}$
	HQderm	$3.77\cdot10^{-4}$- $2.74\cdot10^{-1}$	$1.41\cdot10^{-4}$- $3\cdot10^{-2}$	$1.16\cdot10^{-3}$- $3.03\cdot10^{-1}$	$1.62\cdot10^{-4}$- $7.63\cdot10^{-1}$	$1.48\cdot10^{-2}$- **$3.36\cdot10^{0}$**	$1.31\cdot10^{-2}$- **$1.47\cdot10^{0}$**
	HI	$6.05\cdot10^{-3}$- **$4.39\cdot10^{0}$**	$1.56\cdot10^{-3}$- $3.31\cdot10^{-1}$	$2.73\cdot10^{-3}$- $7.12\cdot10^{-1}$	$3.43\cdot10^{-2}$- **$3.9\cdot10^{1}$**	$1.26\cdot10^{-1}$- **$2.86\cdot10^{1}$**	$1.97\cdot10^{-2}$- **$2.21\cdot10^{0}$**
Children							
	HQing	$1.32\cdot10^{-2}$- **$9.61\cdot10^{0}$**	$3.3\cdot10^{-3}$- $7.03\cdot10^{-1}$	$3.67\cdot10^{-3}$- $9.56\cdot10^{-1}$	$1.68\cdot10^{-4}$- **$2.72\cdot10^{0}$**	$2.6\cdot10^{-1}$- **$5.89\cdot10^{1}$**	$1.54\cdot10^{-2}$- **$1.72\cdot10^{0}$**
	HQinh	$7.24\cdot10^{-7}$- $5.25\cdot10^{-4}$	$8.97\cdot10^{-7}$- $3.84\cdot10^{-5}$	$2\cdot10^{-7}$- $5.23\cdot10^{-5}$	-	$1.42\cdot10^{-5}$- $3.2\cdot10^{-3}$	$8.4\cdot10^{-7}$- $9.42\cdot10^{-5}$
	HQderm	$2.47\cdot10^{-4}$- $1.79\cdot10^{-1}$	$9.25\cdot10^{-5}$- $1.97\cdot10^{-2}$	$7.6\cdot10^{-4}$- $1.98\cdot10^{-1}$	$4.39\cdot10^{-4}$- $4.99\cdot10^{-1}$	$9.72\cdot10^{-3}$- **$2.2\cdot10^{0}$**	$8.61\cdot10^{-3}$- $9.56\cdot10^{-1}$
	HI	$1.32\cdot10^{-2}$- **$9.79\cdot10^{0}$**	$8.44\cdot10^{-3}$- $7.22\cdot10^{-1}$	$3.39\cdot10^{-2}$- **$1.15\cdot10^{0}$**	$6.07\cdot10^{-4}$- **$2.74\cdot10^{0}$**	$2.7\cdot10^{-1}$- **$6.11\cdot10^{1}$**	$2.4\cdot10^{-2}$- **$2.69\cdot10^{0}$**

3. Results and discussion

3.1. Size and mineralogical characteristics of atmospheric particles

This study shows that the number of particles collected on spider webs, their size, and mineralogical composition varied greatly depending on the sample location. For instance, Figure 2a represents the particles of Earth's crust origin (i.e. feldspar, quartz) that can be found adsorbed on the spider web. The sizes of such particles are somewhat bigger than the anthropogenic ones (shown in Figs 2b and 2c). In comparison, smaller particles are represented by the spectrum 4, 5, and 6, where silicate glass with As, sulfides, and silicate glass with Pb, As, Cu, and Zn were noticed (respectively). The presence of such PTEs in these samples indicates anthropogenic activity connected with the activity of the neighboring copper smelter Legnica.

Moreover, the occurrence of the fine fractioned Pb sulfides on the spider webs is also confirmed by SEM images with EDX elemental mapping (Supplementary Fig. S1; in three visible points). However, in some rare cases, the EDX spectra indicate the presence of S and Ca and the

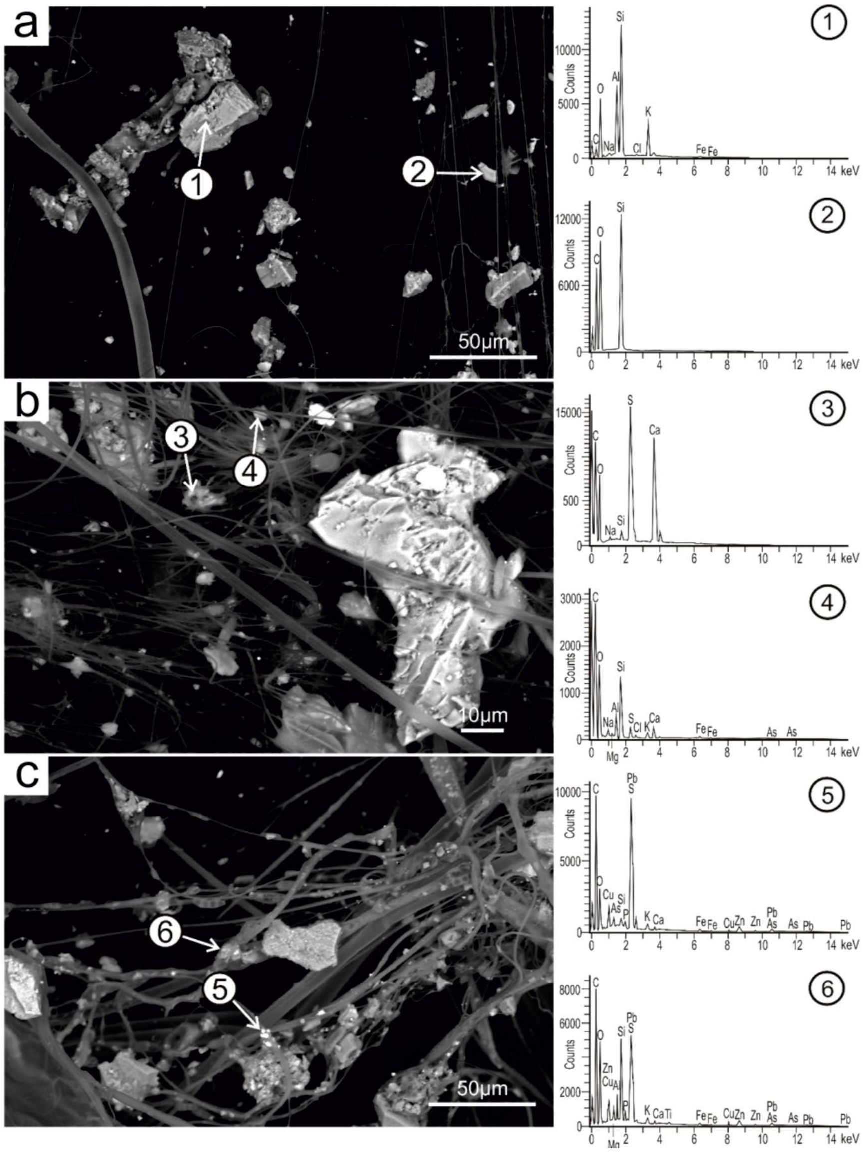

Figure 2. Backscattered electron images of spider web taken from Legnica smelter site (a) 13, (b) 5, and (c) 4 and representative Energy Dispersive X-Ray spectra. Spectrum 1 – K-feldspar, spectrum 2 – quartz, spectrum 3 – gypsum, spectrum 4 – silicate glass with As, spectrum 5 – Sulfides, spectrum 6 – silicate glass with Pb, As, Cu and Zn.

absence of Pb. For these points, the explanation might be the occurrence of sulphur in the form of calcium sulphates (gypsum or anhydrite), probably connected with desulphurization processes occurring in copper smelter Legnica. On the other hand, the adsorption of natural particles on spider webs is confirmed by the presence of big particles of aluminosilicates. The presence of aluminosilicates is in accordance with the geogenic background of the studied area, as clay material occurs in the upper soil layer (Nowicki 2009). Moreover, locally deflated and resuspended geogenic soil material may contain typical crustal (terrigenous) materials like K-feldspar or quartz (Fig. 2a and Supplementary Fig. S1).

Considering the differentiation of mineralogical characteristics of collected particles, eleven groups were recognized, and studied particles were assigned to them (Fig. 3). Three of the first mineralogical phases (terigenic minerals, clay minerals, and other minerals), presented on the graph, are considered terrigenous, and their origin is connected with soil deflation/resuspension, while other groups are thought to be connected with anthropogenic activity (particles derived from industrial and combustion activities). The assignment of the particles into terrigenous or anthropogenic groups was made based on Górka et al. (2020) and Pachauri et al. (2013) but also the character of the local industry and the geological structure in this area were considered. The particles were grouped accordingly, depending on their elemental composition and morphology.

The input of all the distinguished phases was calculated by dividing the number of particles of the selected phase by the total number of particles found on the web. The calculations were done for each sampling point and a specific fraction. This approach allowed assessing the origin of inorganic anthropogenic particles (IAP), which was performed according to the equation below:

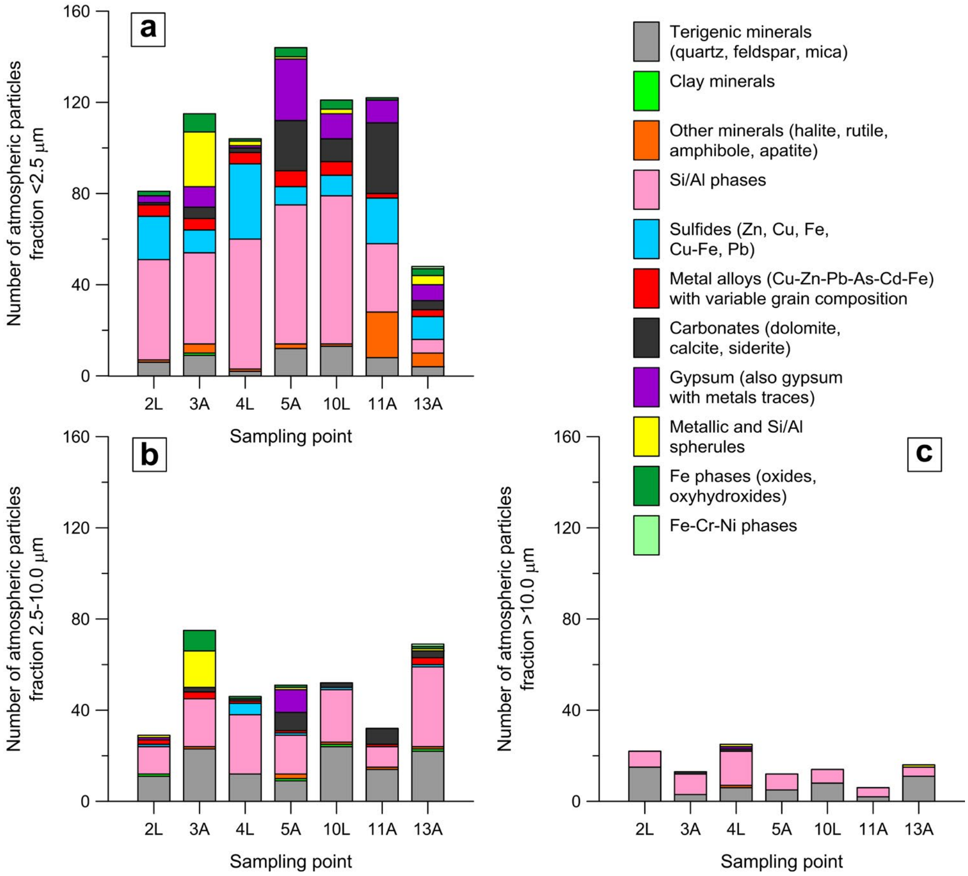

Figure 3. Mineralogical phases reported for particles deposited on spider webs collected in 2018 in the Legnica smelter vicinity. The letter A stands for Agelenidae, and L for Linyphiidae.

%contribution of IAP = (100% - (%Q + %OT)) (7)

where: Q – quartz, OT- other terrigenous minerals.

The natural particles (i.e. crustal material) are usually characterized by bigger sizes, while anthropogenic ones occur rather in finer fractions (WHO 2006). This statement is confirmed in our results (Fig. 3), which show that bigger particles accumulated on the web in smaller amounts are rather undifferentiated and can be identified as the group of terrigenous minerals i.e. silicates and aluminosilicates (Fig. 3c). On the other hand, particles of finer fractions, in general, are more abundant and contain more man-made particles (Figs 3a and b). These finer fractions reveal bigger differentiation in terms of mineralogical composition: commonly including sulfides, metal alloys, Fe phases, metallic and Si/Al spherules which can be an indication of the impact of the local copper smelter. Among these three groups, distinguished by size (<2.5 µm, 2.5-10 µm, >10 µm), the most diverse was the group of the smallest particles (<2.5 µm). Interestingly, in this fraction, in sampling point 3, the highest amount of metallic and Si/Al spherules was present, while in other sampling points, their content was rather negligible. The origin of the Si/Al spherules can be generally connected with the pollution formed in the process of coal burning in the local heat and power stations or coal/wood burning in the furnaces used for home heating (Muszer 2007). However, the temperatures in the furnaces for home heating are probably not high enough for the spherules formation, hence the source of spherules must be the smelter. Moreover, this sampling point (nr 3) is situated directly on the route of dominating wind direction, enhancing the pollution transport from the smelter.

Apart from the groups of natural particles, the $PM_{2.5}$ fraction was generally characterized by a high amount of sulfides which is in accordance with findings by Matassoni et al. (2011), who showed that S-bearing phases occurred mainly in PM_1 and was connected with anthropogenic pollution. The vast majority of sulfides in our work were in the form of anhedral crystals. In contrast, euhedral crystals were relatively rare. The most common sulfides habit is cubic, whereas prismatic crystals were uncommon. The presence of sulfides (especially Cu, Zn, Pb) is typical for the pollution found in the region of Legnica–Głogów Copper District, and it stands in accordance with the findings of Muszer (2007), who characterized similar sulfides in the precipitation collected in the area of Głogów. In our study, the highest amounts of sulfides were noted especially in the points located on the track of prevailing winds (points 2 and 4, located southeast of the smelter), delivering pollution from the smelter. The occurrence of fine fraction sulfides was also observed during spider web biomonitoring of air quality in the vicinity of Głogów city (Bartz et al. 2021).

Also, the appearance of metal alloys was noted in the smallest fraction. Their presence in the collected PM indicates a serious problem with the air quality in the studied area. It underlines that even if the pollution produced has been limited over the past years, the problem is still crucial.

Silica-bearing phases were found commonly in all fractions. However, it is not surprising in this area as they can be delivered by mobilizing small silica grains by convector gases released in copper smelting (i.e. SO_2, N_2, O_2; Muszer 2004). Moreover, similar to Bartz et al. (2021), in many sampling points carbonates, gypsum or metallic and Si/Al spherules occurred, which reveals the impact of the smelter. Usually, gypsum originates from the industrial process in power-pants (i.e. desulphurisation of flue gas; Hao et al. 2017) but some scientists report that it can also have its source in the deterioration of buildings plaster (Bartz et al. 2012; Boev et al. 2013). Also, metal-bearing particles like Fe phases were found in a few sampling points. Fe-rich oxides can be considered an indication of super-local and local pollution, for example, originating from the rail tracks (Matassoni et al. 2011) or destruction and erosion of industrial metal structures. Fe-oxides are one of the most common abrasive components of brakes (Grigoratos, Martini 2014), which may also be an indication of the influence of road traffic pollution. Interestingly, in a few points (e.g. 3, 11, 13), the occurrence of halite was noted. Its presence might be connected with gritting salt used on the roads in the winter, which can still be found in the soils near roads in the summer period. This phenomenon was observed by scientists who indicated that NaCl, commonly used as a de-icing reagent, can be retained in shallow groundwater and soil during wintertime. Subsequently, it can be released in the summer (Kelly et al. 2008). Moreover, the study conducted in Poland also confirms

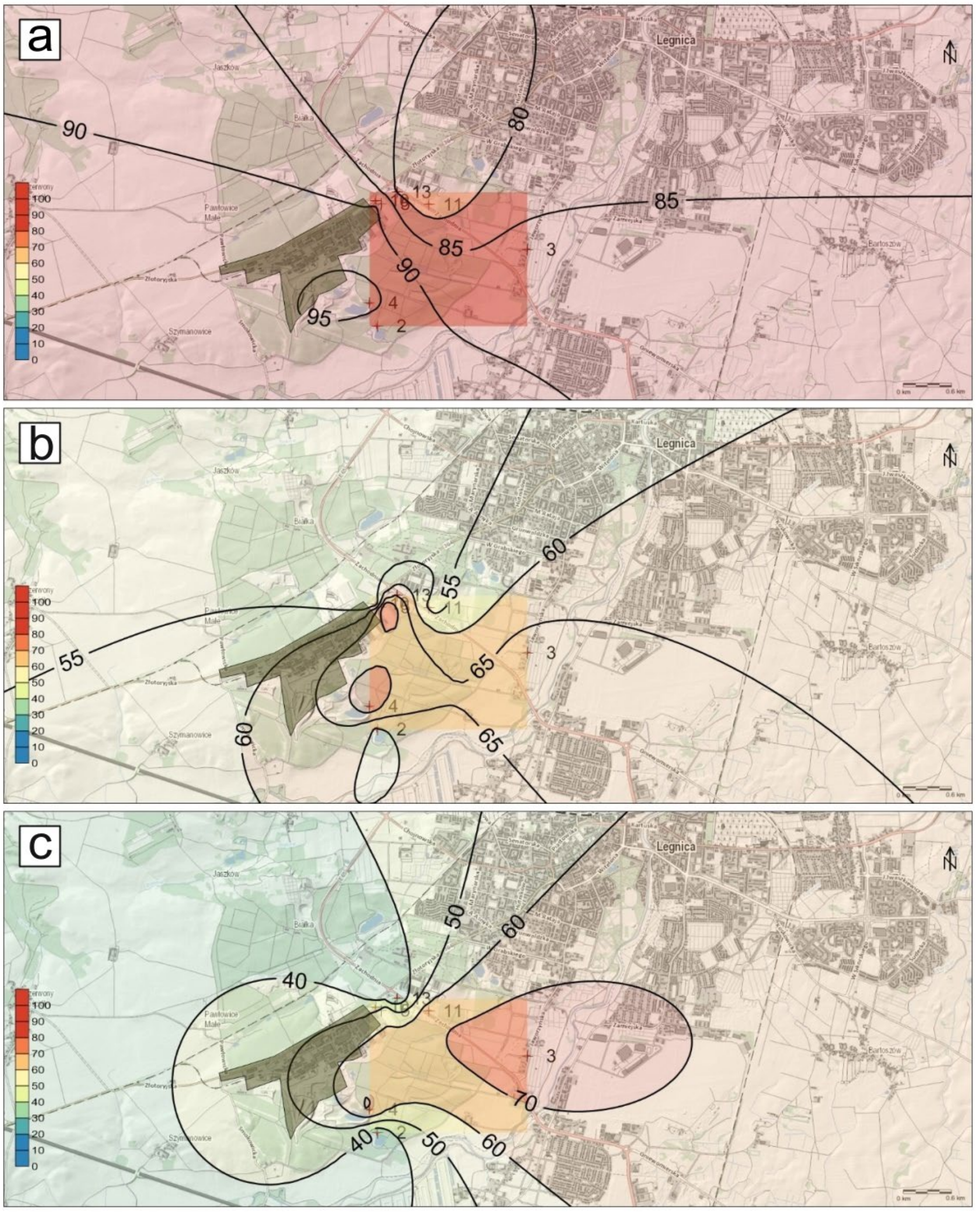

Figure 4. Spatial distribution of anthropogenic atmospheric particles (method of separation presented in the text) fraction (a) $PM_{2.5}$, (b) $PM_{2.5-10}$, and (c) PM_{10} deposited on spider webs in Legnica smelter vicinity. The pale colors mark areas with approximate data (without real sampling points).

that using NaCl in wintertime can result in significantly increased salinity of the soil in samples collected before the winter season up to 6 m from the edge of the road (Marosz 2016).

3.2. Spatial distribution of anthropogenic particles

Different sizes of the particles can, in various degrees, impact human health, and the finest particles are considered more dangerous than coarse ones (Oberdörster et at. 2005). This is due to the fact that smaller fractions, bearing more PTEs, can travel deep into the lung and deposit in the alveoli (Oberdörster et al. 2004). On the other hand, bigger particles are stopped in the nasal area (Kuehl et al. 2012; Oberdörster et al. 2004). Thus, it is very important to know the spatial distribution of specific fractions.

In order to verify the spatial distribution of different particles fractions, maps of the spatial distribution of anthropogenic particles were prepared (Fig. 4). However, the statistical relations between distance from the emitter as well as location/direction of sampling points and amounts of anthropogenic particles do not exist (Supplementary Table S3), which can be due to the existence of some unknown factors or a quite close location of sampling points from the emitter in Legnica copper smelter. Figure 4 shows that PM is transported from the copper smelter to the regions located east of the smelter, according to dominating wind direction (Dancewicz et al. 2009). Normally, bigger particles are likely to be found in the closest area of the emission point, up to a few kilometers, while the range of smaller fractions is supposed to be wider. This spatial distribution was observed during spider web biomonitoring in Głogów (Bartz et al. 2021). Here, however, it can be seen that small particles also settle down close to the emission source (Fig. 4a,b), which is in accordance with the paper of Lv et al. (2020), where it was indicated that smaller particles could also be found close to pollution source. Other possible explanations are aggregations processes of PM with local humidity (e.g. water vapor from industrial processes) which yield faster sedimentation of a bigger conglomerate of PM. It stands in accordance with a previous study in Głogów, where the smallest fraction was also found close to the emitter, but as the sampling area was wider, we could observe their further travel as well (Bartz et al. 2021).

3.3. Analysis of metals collected on spider webs

In order to quantitatively compare our results with other studies, the analysis with the use of ICP-MS was conducted. The statistically tested relations between metals (i.e. Cu and Pb with $\rho = 0.86$; Supplementary Table S3) confirmed Cu-ore genesis connected with ore processing and smelting. Some statistical relations between heavy metals abundance and size of anthropogenic fraction according to our SEM-EDX observations were expected, and data presented in Bartz et al. (2021) for the Głogów copper smelter confirmed it. Unfortunately, this was not statistically confirmed in our study (see Supplementary Table S3) due to the fact that metals probably existed mainly as adsorbed phases on particles (measured by ICP-MS) but were not saved in SEM-EDX. It shows that the PTEs collected on the spider webs varied in amount depending on the sample location (Fig. 5). Generally, our results are quite similar to the previous results of spider web biomonitoring in copper smelting areas (Bartz et al. 2021; Stojanowska et al. 2020), which indicates the main source of pollution (copper smelter). In all of the sampling points commonly occurred Zn, Pb, and Cu while As, Ni, and Cd generally constituted a mi-

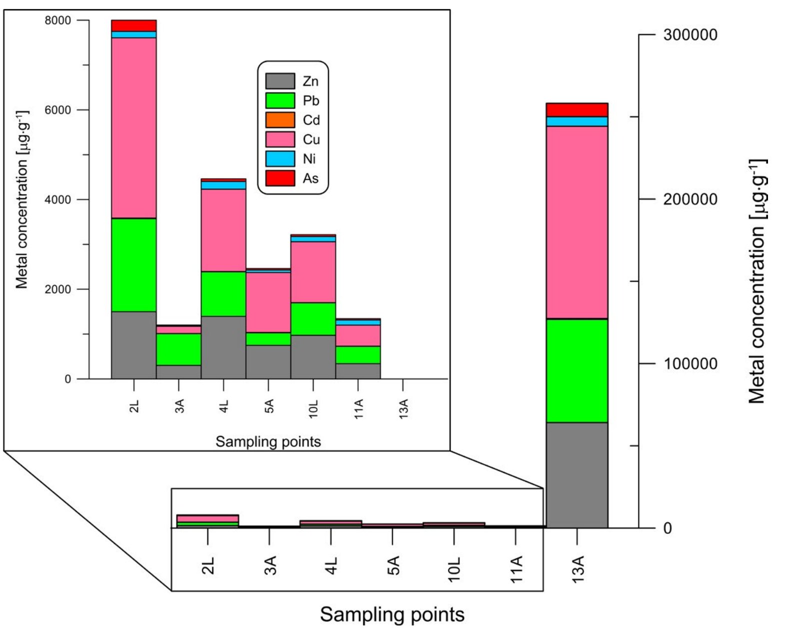

Figure 5. Chemical composition of the samples. The letter A stands for Agelenidae, and L for Linyphiidae.

Table 2. Excess cancer risk for the Legnica smelter area.

ECR/site no.	2	3	4	5	10	11	13
As adults	$1.05\cdot10^{-1}$	$3.03\cdot10^{-3}$	$2.46\cdot10^{-2}$	$1.47\cdot10^{-2}$	$1.74\cdot10^{-2}$	$1.25\cdot10^{-2}$	$3.45\cdot10^{0}$
As children	$1.62\cdot10^{-1}$	$2.52\cdot10^{-2}$	$1.93\cdot10^{-1}$	$6.21\cdot10^{-2}$	$1.32\cdot10^{-1}$	$1.29\cdot10^{-1}$	$6.57\cdot10^{0}$
Ni adults	$3.68\cdot10^{-3}$	$5.72\cdot10^{-4}$	$4.38\cdot10^{-3}$	$1.41\cdot10^{-3}$	$2.99\cdot10^{-3}$	$2.93\cdot10^{-3}$	$1.49\cdot10^{-1}$
Ni children	$9.8\cdot10^{-3}$	$1.52\cdot10^{-3}$	$1.17\cdot10^{-2}$	$3.75\cdot10^{-3}$	$7.98\cdot10^{-3}$	$7.82\cdot10^{-3}$	$3.98\cdot10^{-1}$
Pb adults	$2.46\cdot10^{-3}$	$8.35\cdot10^{-4}$	$1.18\cdot10^{-3}$	$3.28\cdot10^{-4}$	$8.57\cdot10^{-4}$	$4.56\cdot10^{-4}$	$7.42\cdot10^{-2}$
Pb children	$6.55\cdot10^{-3}$	$2.23\cdot10^{-3}$	$3.14\cdot10^{-3}$	$8.75\cdot10^{-4}$	$2.29\cdot10^{-3}$	$1.22\cdot10^{-3}$	$1.98\cdot10^{-1}$
Cd adults	$2.72\cdot10^{-3}$	$8.77\cdot10^{-3}$	$1.16\cdot10^{-3}$	$1.68\cdot10^{-3}$	$8.3\cdot10^{-4}$	$8.4\cdot10^{-4}$	$9.31\cdot10^{-2}$
Cd children	$7.26\cdot10^{-3}$	$2.34\cdot10^{-3}$	$3.09\cdot10^{-3}$	$4.47\cdot10^{-3}$	$2.21\cdot10^{-3}$	$2.24\cdot10^{-3}$	$2.48\cdot10^{1}$

Table 3. Summary of data on metals concentration in road dust for other countries in relation to our studies with spider webs [mg/kg]. The highest concentrations for the study are shown.

Site	Ni	Cu	Zn	As	Pb	Cd	References
Kumasi, Ghana	44.1	50.2	280.3	6.2	46.9	-	Nkansah et al. (2017)
Muskat, Oman	9	68.2	181.1	5.4	19.4	-	Al-Shidi et al. (2022)
Luanda, Angola	10	42	317	5	351	1.1	Ferreira-Baptista, De Miguel (2005)
Legnica, Poland (min.- max.)	22.3-5813.6	161-116900.8	301.5-64125.5	7.15-8138	277.2-62725.9	4.68-524.2	This study

nority. Given that the emission sources of As (e.g. smelters) elevate the risk of lung cancer (WHO 2019), its concentration, even if not as high as other elements, should not be omitted. Interestingly, in point number 13, exceptionally high concentrations were noted. In this point, the Cu concentration dominated, followed then by Pb and Zn and much smaller quantities of As and Ni. The elements concentration can be explained by the specific location of site 13, where the impact of both: communication (located near busy crossroads) and industrial (proximity of smelter) sources can be observed. What is more, in the neighboring street, demolition and construction works were carried out during the sampling period, which can additionally influence this distinct element concentration.

3.4. The assessment of health risk

3.4.1. Exposure dose

Health risk assessment based on concentrations of elements in spider webs was calculated and presented in Table 1 and Supplementary Tables S4-S9, where ADDing - Average Daily Dose for ingestion, ADDinh - Average Daily Dose for inhalation, ADDderm - Average Daily Dose for the dermal route. In general, the highest concentrations of metals can be absorbed via the oral route. The maximum dose was obtained for Cu, Zn, and Pb at site 13; ADDing for children was $3.84\cdot10^{5}$ mg/kg for Cu, $2.11\cdot10^{5}$ mg/kg for Zn, and $2.06\cdot10^{5}$ mg/kg for Pb (Table 1 and Supplementary Tables S4, S5 and S8). The minimal amount of studied metals were absorbed by inhalation. The minimum dose was recorded for adults for As: ADDinh = $7.25\cdot10^{-4}$ mg/kg (site 3) and for Cd: ADDinh = $4.74\cdot10^{-4}$ mg/kg (site 10). For children, it was respectively for As: ADDinh = $1.29\cdot10^{-3}$ mg/kg (site 3), Cd: ADDinh = $8.51\cdot10^{-4}$ mg/kg (site 10). ADD for children via the oral route is almost two times higher than for adults, and the values were the highest in relation to other exposure routes (Table 1 and Supplementary Tables S4-S9). ADD via oral and inhalation routes is about two times higher for children than adults, suggesting that children are the most sensitive group (Voutsa et al. 2015).

3.4.2. Non-cancerogenic health risk assessment

The results show that the greatest health risk is caused by pollutants that are ingested as HQing values were greater than 1 for elements such as Cu, As, and Pb (Table 1), often for both groups: children and adults. HQderm values exceeded 1 for Pb (children and adults) and As (adults). On the other hand, values greater than 1 were not recorded for HQ via the inhalation route. What is interesting, the highest values were obtained mainly for only one site (site 13, Table 1 and Supplementary Tables S4-S9). The overall HI values for studied metals exceed 1 for Cu (adults and children), As (adults), Ni (children), Pb (adults and children), and Cd (adults and children). The results indicate the high harmfulness of metals, especially at site 13.

3.4.3. Cancer risk assessment

Calculations of the ECR are presented in Table 2. Almost all sites were characterised by high carcinogenic risks (>10^{-4}). Although, a low risk of cancer (ECR = 10^{-4}) was recorded for sites 3, 5, 10, and 11 (for Pb adults), for site 5 (for Pb children), and sites 10 and 11 (Cd adults). High risk was recorded at site 13, consistent with previous findings (see HQ and HI, Table 1).

The comparison of these values with other findings is quite difficult as studies based on the pollution collected on spider webs have never been conducted. Hence, we decided to compare our results with the data obtained for road dust (Table 3). At first, the concentrations of collected PTEs were compared as this is the main factor influencing the health risk calculation. In the area of the Legnica smelter, point 13 was characterized by the highest concentrations of metals, which highly impacted the obtained results. However, the lowest values obtained for the studied region were comparable with other studies (Table 3). Such differentiation is quite surprising but difficult to explain due to the fact that in the case of road dust the accumulation time of the particles is unknown. Due to such differentiation in PTEs concentration, the results of HQ were distinct as well. In some cases, the results of HQ for Legnica were much higher than in other studies. For instance, as reported by Nkansah et al. (2017), the non-carcinogenic risk value for As for adults was HQing = $3.5 \cdot 10^{-2}$ (Nkansah et al. 2017), while for our studies (point 13), this value was much higher (HQing = $3.8 \cdot 10^{1}$). Similarly, higher results of HI in point 13 were obtained in the case of Pb for children (HI = $6.11 \cdot 10^{1}$) when compared to studies in the capital of Oman, Muscat (HI = $1.2 \cdot 10^{-2}$). Having in mind that in our study the results were several times greater than those obtained for other places, there might exist a serious risk in our study area. Nevertheless, one should remember that other sites examined in this study show lower values than those in point 13. Among these four different places, inhabitants of Legnica agglomeration living near site 13 (busy crossroads: road 323 and S3) are more exposed to a negative impact of Pb on health than the inhabitants of other cities.

4. Conclusions

This research has shown the usefulness of spider webs in air quality monitoring. Based on the deposited PM, the assessment of health risks for humans living near sources of contamination can be performed. A comparative assessment shows that carcinogenic and non-carcinogenic risks are among the highest reported in the world (especially in some sampling points). Considering both conducted analyses (SEM-EDX and ICP-MS), we claim that the impact of the Legnica copper smelter is notable and can be observed mainly on the leeward side. SEM-EDX analysis confirmed that collected PM was differentiated: PM_{10} was dominated by the particles of natural origin while fine fractions were composed of diverse anthropogenic particles, whose origin can be mainly connected with the activity of the copper smelter and in smaller quantity with the road traffic. These results indicate that SEM-EDX analyses of PM collected on spider webs can help in identifying the possible sources of pollution in the studied area.

Our findings could simplify, speed up, and greatly lower the cost of such studies as spider webs are ubiquitous and easy to collect. The study, even if conducted only on a local scale, is believed to give satisfying results elsewhere.

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Conflicts of interest

The authors have no conflicts of interest to declare.

Supplementary Material

Supplementary data to this article can be found online at https://doi.org/10.2478/mipo-2022-0004.

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