Politechnika Wrocławska

Wydział Inżynierii Środowiska

ROZPRAWA DOKTORSKA

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Ocena skuteczności zastosowania sieci pajęczych poprzez wykonanie badań porównawczych (pyłomierz vs. sieci pajęcze) przy ocenie jakości powietrza wybranego regionu.

Promotorzy:

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Niniejsza rozprawa doktorska ma charakter interdyscyplinarny i zrealizowana została w ramach dyscyplin: Inżynieria Środowiska, Górnictwo i Energetyka oraz Nauki o Ziemi i Środowisku.

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Spis treści

Streszczenie

Zanieczyszczenie powietrza jest jednym z większych problemów, z jakimi obecnie musi mierzyć się ludzkość. Nawet jeśli podejmowane są liczne próby, mające na celu ograniczenie emisji zanieczyszczeń, to wyeliminowanie ich całkowicie jest właściwie niemożliwe. Biorąc pod uwagę powyższy fakt poszukiwanie nowych, tanich i łatwo dostępnych metod monitoringu jakości powietrza stało się niezwykle ważne. Jednakże, zanim nowe metody zostaną wprowadzone do użytku należy się upewnić, że odpowiedź środowiskowa na temat jakości powietrza uzyskiwana z ich pomocą jest wiarygodna. Niniejszy autoreferat składa się z cyklu jednolitych tematycznie publikacji, dotyczących możliwości wykorzystania m.in. sieci pajęczych oraz innych metod przy monitoringu jakości powietrza. Wszystkie badania prowadzone były w latach 2018-2021. Do badań wykorzystano sieci pająków (głównie z rodziny Agelenidae), pobrane z hodowli laboratoryjnej i następnie transplantowane w terenie oraz uzupełniająco sieci pobrane bezpośrednio w terenie. Jako drugi bioindykator wybrany został gatunek porostu pustułka pęcherzykowata - *Hypogymnia physodes* (L.), który transplantowano ze Stobrawskiego Parku Krajobrazowego. Oprócz wymienionych wcześniej bioindykatorów do przeprowadzanych badań wykorzystany został również specjalistyczny sprzęt używany w metodach aktywnych , tj. pyłomierz DIGITEL DHA 80 oraz pyłomierz z analizatorem metali online - HORIBA PX-375. Głównym celem pracy było zweryfikowanie, czy dane o jakości powietrza otrzymywane z pasywnych badań biomonitoringowych, np. z wykorzystaniem sieci pajęczych, są zbliżone do standardowego monitoringu z wykorzystaniem metod aktywnych. Co więcej, ważne było też bezpośrednie porównanie stężeń metali uzyskanych z analiz sieci pajęczych z tymi, odnotowanymi dla porostów. Ponadto, zbadano możliwości wykorzystania danych o cząstkach zakumulowanych na sieciach pajęczych do oceny ryzyka zdrowotnego. Oprócz krótkookresowych badań biomonitoringowych przeprowadzony został także roczny monitoring zanieczyszczeń powietrza z wykorzystaniem różnorodnych analiz, mający na celu szczegółowe scharakteryzowanie jakości powietrza na obszarze w okolicach huty miedzi Legnica.

Przeprowadzenie wyżej wymienionych badań wykazało, że wybrane metody oceny zanieczyszczenia powietrza (tj. biomonitoring z wykorzystaniem sieci pajęczych i porostów oraz metoda aktywna) dają zbliżoną do siebie odpowiedź dotycząca źródeł zanieczyszczeń. Dodatkowo, uzyskano informację, iż akumulacja metali przez sieci pajęcze jest wyższa od akumulacji przez porosty, a co więcej cząsteczki zakumulowane na sieciach pajęczych mogą być z powodzeniem wykorzystywane przy ocenie ryzyka zdrowotnego. Finalnie, można

stwierdzić, iż sieci pajęcze, jako tani i łatwo dostępny bioindykator, mogą zostać uznane za użyteczne narzędzie w biomonitoringu jakości powietrza.

Summary

Air pollution is one of the biggest issues that humanity is facing today. Even if numerous attempts are made to reduce the emission of pollution, it is practically impossible to eliminate them completely. Considering the above, the search for new, cheap and easily accessible methods of air quality monitoring has become extremely important. However, before new methods come into use, it is important to make sure that the answer they give about air quality is trustworthy. This self-report consists of a series of thematically uniform publications, concerning, among others, the possibility to use spider webs and different methods in the air quality monitoring. The research was conducted in 2018-2021. Spider webs (mainly from the Agelenidae family), collected from laboratory reared spiders and then transplanted in the study area were used for this research, and supplementary webs directly from the field were taken. Lichens – species *Hypogymnia physodes* (L.), which were transplanted from the Stobrawa Landscape Park, were selected as the second bioindicator. In addition to the previously mentioned bioindicators, specialized equipment for active methods was also used for these studies, i.e. the DIGITEL DHA 80 high volume sampler and the HORIBA PX-375 sampler with the online metal analyzer. The main objective of this work was to verify whether information on air quality obtained from passive biomonitoring methods, for example, using spider webs is similar to the response from monitoring using active methods. Moreover, it was also important to directly compare the concentrations of metals received from the analyses of spider webs with those recorded for lichens. An additional part of the work was devoted to examining the possibility of using particles accumulated on the spider webs in the assessment of health risk. Apart from the short-term biomonitoring studies, annual air pollution monitoring was also carried out using various analyses, aimed at detailed characterization of air quality in the area close to the Legnica copper smelter. The research has shown that the chosen methods for air pollution monitoring (i. e. biomonitoring with the use of spider webs and lichens and active method) give similar responses in terms of the sources of air pollution. In addition, it was concluded that the accumulation of metals by spider webs was higher than that by lichens and, what is more, that the particles collected by spider webs can be successfully used for the assessment of health risk. Finally, it can be said that spider webs, as a cheap and easily accessible bioindicator, can be considered a useful tool in air quality biomonitoring.

1. **Posiadane dyplomy, stopnie naukowe/ artystyczne – z podaniem nazwy, miejsca i roku ich uzyskania oraz tytułu rozprawy**

- 2016 r., dyplom licencjata: kierunek: geologia, Wydział Nauk o Ziemi i Kształtowania Środowiska, Uniwersytet Wrocławski;
  Tytuł pracy: „Litologia i struktura sejsmiczna klina płaszcza nad subdukującą płytą", promotor: prof. dr hab. Jacek Puziewicz
- 2018 r., dyplom magistra: kierunek: geologia, Wydział Nauk o Ziemi i Kształtowania Środowiska, Uniwersytet Wrocławski;
  Tytuł pracy: „Ocena jakości powietrza w Świętokrzyskim Parku Narodowym na podstawie analiz geochemicznych i izotopowych węgla zawartego w pyle atmosferycznym z wykorzystaniem bioindykatora *Abies alba"*, promotor: dr hab. Maciej Górka, prof. UWr.

2. **Wskazanie osiągnięcia wynikającego z art. 16 ust. 2 ustawy z dnia 14 marca 2003 r. o stopniach naukowych i tytule naukowym oraz o stopniach i tytule w zakresie sztuki (Dz. U. nr 65, poz. 595 ze zm.)**

Osiągnięcie naukowe stanowi cykl publikacji składający się z ośmiu oryginalnych prac o łącznej punktacji MNiSW: 790 pkt. oraz IF: 32,738.

1) *The use of spider webs in the monitoring of air quality - a review.* **Agnieszka Stojanowska**, Farhad Zeynalli, Magdalena Wróbel, Justyna Rybak. *Integrated Environmental Assessment and Management*. 2022, vol. 17, nr 1, s. 1-13.
   Udział własny: opracowanie koncepcji artykułu, przegląd literaturowy, udział w przygotowaniu tekstu manuskryptu i redagowanie finalnej wersji publikacji
   IF: 2,992
   Punktacja MNiSW: 70 pkt.

2) *The impact of seasonality and meteorological conditions on $PM_{2.5}$ carbonaceous fractions coupled with carbon isotope analysis: advantages, weaknesses and interpretation pitfalls.* Maciej Górka, **Agnieszka Trzyna**, Anita Lewandowska, Anetta Drzeniecka-Osiadacz, Beata Miazga, Justyna Rybak, David Widory. *Atmospheric Research*. 2023, vol. 290, art. 106800, s. 1-17.

Udział własny: przegląd literaturowy, sformułowanie problemu badawczego, dostarczenie materiału do badań, opracowanie metodologii, nadzór nad projektem, pozyskanie wsparcia finansowego, udział w przygotowaniu tekstu manuskryptu

IF: 5,965

Punktacja MNiSW: 100 pkt.

3) *Spider webs and lichens as bioindicators of heavy metals: a comparison study in the vicinity of a copper smelter (Poland).* **Agnieszka Stojanowska**, Justyna Rybak, Marta Bożym, Tomasz Olszowski, Jan Stefan Bihałowicz. *Sustainability*. 2020, vol. 12, nr 19, art. 8066, s. 1-13.

   Udział własny: sformułowanie problemu badawczego, przegląd literaturowy, dostarczenie materiału do badań, opracowanie koncepcji artykułu, wizualizacja danych, nadzór nad projektem, przygotowanie tekstu manuskryptu i redagowanie finalnej wersji publikacji

   IF: 3,251

   Punktacja MNiSW: 100 pkt.

4) *Air pollution research based on spider web and parallel continuous particulate monitoring - a comparison study coupled with identification of sources.* **Agnieszka Stojanowska,** Tomasz Mach, Tomasz Olszowski, Jan Stefan Bihałowicz, Maciej Górka, Justyna Rybak, Małgorzata Rajfur, Paweł Świsłowski. *Minerals*. 2021, vol. 11, nr 8, art. 812, s. 1-20.

   Udział własny: sformułowanie problemu badawczego, przegląd literaturowy, dostarczenie materiału do badań, nadzór nad projektem, opracowanie koncepcji artykułu, udział w przygotowaniu tekstu manuskryptu i redagowanie finalnej wersji publikacji

   IF: 2,644

   Punktacja MNiSW: 100 pkt.

5) *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.* Wojciech Bartz, Maciej Górka, Wojciech Bartz, Justyna Rybak, Radosław Rutkowski, **Agnieszka Stojanowska.** *Chemosphere*. 2021, vol. 278, art. 130454, s. 1-14.

Udział własny: opracowanie koncepcji artykułu, udział w przygotowaniu tekstu manuskryptu

IF: 8,943

Punktacja MNiSW: 140 pkt.

6) *Health risk assessment in the vicinity of a copper smelter: particulate matter collected on a spider web.* **Agnieszka Trzyna**, Justyna Rybak, Wojciech Bartz, Maciej Górka. *Mineralogia*. 2022, vol. 53, s. 36-50.

   Udział własny: sformułowanie problemu badawczego, przegląd literaturowy, opracowanie koncepcji artykułu, przygotowanie tekstu manuskryptu i redagowanie finalnej wersji publikacji

   Punktacja MNiSW: 70 pkt.

7) *Biomonitoring z wykorzystaniem sieci pajęczych – jakość powietrza i ocena narażenia zdrowotnego.* **Agnieszka Trzyna**, Justyna Rybak. *Zeszyty Naukowe SGSP*. 2022, nr 82, s. 7–19.

   Udział własny: sformułowanie problemu badawczego, dostarczenie materiału do badań, przegląd literaturowy, opracowanie koncepcji artykułu, analiza i wizualizacja danych, przygotowanie tekstu manuskryptu i redagowanie finalnej wersji publikacji

   Punktacja MNiSW: 70 pkt.

8) *Comparison of active and passive methods for atmospheric particulate matter collection: From case study to a useful biomonitoring tool*. **Agnieszka Trzyna**, Justyna Rybak, Maciej Górka, Tomasz Olszowski, Joanna A. Kamińska, Tomasz Węsierski, Małgorzata Majder-Łopatka. *Chemosphere*. vol. 334, art. 139004, s. 1-11.

   Udział własny: przegląd literaturowy, sformułowanie problemu badawczego, dostarczenie materiału do badań, opracowanie metodologii, analiza i wizualizacja danych, nadzór nad projektem, opracowanie koncepcji artykułu, udział w przygotowaniu tekstu manuskryptu i redagowanie finalnej wersji publikacji

   IF: 8,943

   Punktacja MNiSW: 140 pkt.

Artykuł	Czynnik wpływu (IF)	Punktacja MNiSW
1	2,92	70
2	5,965	100
3	3,251	100
4	2,644	100
5	8,943	140
6	---	70
7	---	70
8	8,943	140
SUMA	32,738	790

3. Omówienie celu naukowego ww. pracy i osiągniętych wyników

3.1. Tło problemu

Pomimo ciągłych prac nad poprawą jakości powietrza, problem ten jest wciąż jednym z największych wyzwań środowiskowych w Europie (EEA, 2021). Sprawa jest istotna, ponieważ zanieczyszczenia powietrza mają bezpośredni wpływ na zdrowie ludzi, prowadząc do różnych chorób, m.in. płuc i oskrzeli, a także do zaostrzenia objawów astmy (EEA, 2021). Zgodnie z raportem Europejskiej Agencji Środowiskowej (EEA) pył zawieszony, jako główna substancja zanieczyszczająca powietrze, odpowiada za około 307 000 przedwczesnych zgonów wśród obywateli Unii Europejskiej (EEA, 2022). Na tle krajów europejskich niekorzystnie wyróżnia się Polska, gdzie jakość powietrza jest dość często nieodpowiednia i prowadzi do przekroczenia wyznaczonych norm (EEA, 2020).

Ocena jakości powietrza, która jest pierwszym krokiem w walce o lepszą jakość środowiska, opiera się zazwyczaj o punkty monitoringu w stałej lokalizacji, w których do pomiarów stężeń substancji zanieczyszczających używany jest specjalistyczny sprzęt (tj. pyłomierze i analizatory gazu etc.). Jednakże, biorąc pod uwagę wagę problemu związanego z jakością powietrza w krajach europejskich, zagęszczenie takich stacji monitoringowych w terenie jest obecnie niewystarczające (WHO, 2021). Zwiększenie liczby stacji monitoringowych wiąże się z dużymi kosztami inwestycyjnymi m.in. ze względu na konieczność zakupienia nowego sprzętu czy zatrudnienia większej liczby osób do jego obsługi. Potrzebne są więc proste, szybkie i tanie rozwiązania dostarczające wiarygodnej informacji o stanie powietrza w danej lokalizacji. Co więcej, pojawia się również potrzeba dostępu do narzędzi, które można wykorzystywać w ograniczonych warunkach dostępności infrastruktury (np. elektryczności), m.in. w górach czy na obszarach mocno zalesionych. Dodatkowo, w takich warunkach nie zawsze możliwe jest umieszczenie specjalistycznego sprzętu, który ze względu na swoją wartość ekonomiczną lub konieczność systematycznej obsługi nie może pozostać bez całkowitego nadzoru na dłuższy czas. Oczywiste jest, że metody referencyjne są metodami najbardziej precyzyjnymi, jednakże z uwagi na ich specyfikę, poszukiwanie innych, tańszych rozwiązań do monitorowania jakości powietrza staje się skrajnie istotne.

Rozwiązaniem tego problemu jest biomonitoring, czyli metoda wykorzystania organizmów żywych (lub ich części) w celu uzyskania informacji na temat stanu środowiska (Markert et al., 2003). Wykorzystanie takich materiałów do badań pozwala na zaplanowanie wielu punktów pomiarowych bez użycia dużych nakładów finansowych (Kłos et al., 2018; Markert, 2007). W ocenie jakości powietrza najczęściej wykorzystuje się porosty (Ciężka et al., 2018;

Massimi et al., 2019), mchy (Kosior et al., 2008; Maxhuni et al., 2016), a także igły i liście drzew (Górka et al., 2020; Stojanowska et al., 2021). W ostatnim czasie coraz większą popularność zyskały także sieci pajęcze (Górka et al., 2018; Rybak et al., 2015; van Laaten et al., 2020). Są one dobrym narzędziem środowiskowym ze względu na możliwość akumulowania na swojej powierzchni aerozoli atmosferycznych (Hose et al., 2002; Rachwał et al., 2018; Rybak i Olejniczak, 2014; Xiao-li et al., 2006). Co więcej, sieci pajęcze są materiałem tanim i łatwo dostępnym, co znacząco ułatwia ich stosowanie w monitoringu środowiska.

Pierwsze badania wykorzystujące sieci pajęcze do oceny zanieczyszczeń powietrza opublikowano w 2002 roku (Hose et al., 2002). Sieci użyto jako indykator zanieczyszczenia powietrza przez Pb oraz Zn w Jaskiniach Jenolan w Australii. W pracy wykazano, że jaskinie Jenolan charakteryzowały się podwyższonym stężeniem Pb i Zn w porównaniu do dwóch innych jaskiń, stanowiących miejsca referencyjne. Zidentyfikowane zanieczyszczenia zostały powiązane z emisją pochodzącą z transportu, a sieci pajęcze po raz pierwszy uznano za użyteczne w ocenie pochodzenia zanieczyszczeń.

Kolejno temat kontynuowano w Chinach, gdzie sieci pajęcze zostały ponownie wykorzystane jako indykator zanieczyszczeń powiązanych z ruchem drogowym (Xiao-li et al., 2006). Zauważono istotne różnice w zawartości pierwiastków potencjalnie toksycznych akumulowanych na sieciach zebranych z obszarów zanieczyszczonych, w porównaniu do tych z miejsc referencyjnych, a zróżnicowanie to powiązano z odległością od dróg. Po przetestowaniu sieci pajęczych w monitoringu, Xiao-li wraz z zespołem celnie zauważyli konieczność sprawdzenia powiązań pomiędzy zanieczyszczeniami obserwowanymi w środowisku, a tymi oznaczonymi na sieciach pajęczych.

Dalsze lata przyniosły znaczny rozwój tematyki biomonitoringu z wykorzystaniem sieci pajęczych do oceny stopnia zanieczyszczenia powietrza atmosferycznego, z czego sporą część tych badań przeprowadzono w Polsce (e.g. Ayedun et al., 2013; Rybak, 2015; Rybak et al., 2019b, 2012; Yalwa and Kabo, 2015). Powyższe prace udowodniły, że materiał ten może być użyteczny przy ocenie zanieczyszczenia powietrza wielopierścieniowymi węglowodorami aromatycznymi (Rutkowski et al., 2019; Rybak i Olejniczak, 2014; Rybak, 2014; Rybak et al., 2019) i pierwiastkami potencjalnie toksycznymi (Hose et al., 2002; Rybak et al., 2015; Rybak, 2015; Xiao-li et al., 2006), a także przy ocenie właściwości genotoksycznych i mutagennych pyłu zakumulowanego na sieciach pajęczych (Rutkowski et al., 2018; Rutkowski et al., 2019). Jednakże porównanie otrzymanych wyników z monitoringu pasywnego z wynikami z aktywnego monitoringu powietrza w celu zweryfikowania, czy informacja uzyskana z analizy sieci jest zgodna z faktycznym ilościowym i jakościowym zanieczyszczeniem powietrza, nie zostało jeszcze dokładnie rozpoznane. W momencie rozpoczynania prac badawczych nad tą dysertacją, sieci pajęcze nie były też nigdy wcześniej porównywane z innymi bioindykatorami.

3.2. Cel pracy oraz hipoteza badawcza

Głównym celem pracy była ocena skuteczności zastosowania sieci pajęczych w monitoringu powietrza. Cel ten zrealizowano poprzez wykonanie analizy porównawczej dwóch metod wykorzystywanych do oceny jakości powietrza. Analiza porównawcza dotyczyła zestawienia metody aktywnej (konwencjonalnej, powszechnie stosowanej) wykorzystującej pyłomierz i referencyjną metodę grawimetryczną z metodą pasywną, tj. z sieciami pajęczymi. Celem pobocznym pracy było porównanie dwóch narzędzi wykorzystywanych w biomonitoringu: powszechnie stosowanych porostów (w oparciu o gatunek pustułki pęcherzykowatej) oraz stosunkowo nowego bioindykatora, tj. sieci pajęczych. Dodatkowym, ale również bardzo istotnym, celem pracy był rozwój metody wykorzystywania sieci pajęczej jako narzędzia biomonitoringowego, a także analiza zanieczyszczeń pyłowych i ocena ryzyka zdrowotnego wśród mieszkańców na badanym obszarze.

Hipoteza badawcza zakłada, że wyniki otrzymane z badań wykorzystujących rekomendowaną metodę grawimetryczną z proponowaną nowatorską metodą biomonitoringu za pomocą sieci pajęczych są zgodne i dają tę samą odpowiedź co do źródła zanieczyszczeń, choć niekoniecznie muszą być to takie same wyniki w charakterze ilościowym.

3.3. Metodyka

Badania nad wskazaną tematyką przeprowadzono w latach 2018-2021. Obszar badań stanowiły głównie tereny związane z działalnością przemysłową hut miedzi (Legnica, Głogów), a dodatkowo część z badań prowadzono na obszarze miejskim (Wrocław) oraz wiejskim (Kotórz Mały k/Opola).

Na potrzeby badań biomonitoringowych wybrane zostały pająki z rodziny lejkowcowatych (Agelenidae). Zazwyczaj występują one wśród gęstej roślinności, w dziuplach oraz szczelinach drzew. Swoje sieci łowne budują tuż przy powierzchni ziemi lub w niskich trawach. Gatunki synantropijne pojawiają się z kolei w piwnicach, łazienkach, na strychach i w kątach mieszkań. Osobniki z rodziny Agelenidae nie są agresywne, a ich jad nie stanowi zagrożenia dla człowieka (Jäger i Żabka, 2008). Nić przędna, którą produkują, jest wynikiem zakrzepnięcia wydzieliny białkowej kądziołków przędnych. Mechanizm zamiany ciekłej wydzieliny, rozpuszczalnej w wodzie w litą jedwabną nić nie jest do końca dobrze poznany. Wiadomo jednak, że cząsteczki łańcucha polipeptydowego przechodzą zmianę orientacji z rozpuszczalnej α-konfiguracji w nierozpuszczalną konfigurację β. Nić pajęcza jest więc włóknem białkowym, składającym się z nieuporządkowanych łańcuchów aminokwasów (konfiguracja α) i uporządkowanych pofałdowanych płacht, tworzących kryształy białek (konfiguracja β). Uporządkowane płachty nadają sieci pajęczej wytrzymałość, natomiast luźne łańcuchy aminokwasów sprawiają, że jest ona elastyczna (Vollrath, 1992).

Rodzina Agelenidae składa się z 94 rodzajów, wśród których wyróżnia się 1380 gatunków, a ich występowanie ma zasięg globalny (World Spider Catalog, 2023), dzięki czemu ich sieci są łatwo dostępne. Kolejną zaletą pająków z tej rodziny jest to, że budują gęstą, nieregularną sieć w postaci płachty o pokaźnych rozmiarach (Roberts, 1993), a co najważniejsze nie zjadają zbudowanej wcześniej sieci. Ostania z wymienionych cech umożliwia dokładne określenie czasu ekspozycji sieci na zanieczyszczenia, co nie jest możliwe w przypadku pająków np. z rodziny Araneidae, które mają zwyczaj zjadania swoich starych, zniszczonych sieci. Dodatkowo, fakt, że wybrane pająki nie mają nawyku zjadania wyprodukowanej pajęczyny sprawia, że możliwa jest ich hodowla laboratoryjna, dzięki której otrzymuje się czystą, niezanieczyszczoną pyłami atmosferycznymi sieć (Górka et al., 2018) z możliwością transplantowania jej na wybranym obszarze badań.

W przeprowadzonych badaniach wykorzystano sieci pajęcze uzyskane głównie z laboratoryjnej hodowli pająków. Agelenidae hodowane były pojedynczo w specjalnych szklanych terrariach. Dno pojemników wypełnione było ziemią kokosową, zwilżaną systematycznie, by zapewnić odpowiednią wilgotność. Przez cały okres prowadzenia badań pojemniki z pająkami znajdowały się w temperaturze pokojowej (D:25°C, N:15°C). Pająki karmiono muszkami owocówkami pozbawionymi skrzydeł (*Drosophila hydei)* oraz larwami mącznika młynarka (*Tenebrio molitor*). Czyste sieci (sieci zerowe) pozyskiwane były regularne, a częstotliwość ich zbierania uzależniona była od produktywności pająków. Wyprodukowaną przez pająki sieć rozciągano na powierzchnię szalki Petriego i szczelnie zamkniętą przechowywano, aż do momentu wykorzystania. W dniu rozpoczęcia eksperymentu szalki Petriego z sieciami rozmieszczano w terenie w wybranych punktach badawczych, przytwierdzając szalkę do sztywnej powierzchni za pomocą kleju. Uzupełniająco użyte zostały sieci pobrane *in situ*. Znalezione sieci były niszczone na początku trwania eksperymentu, a czas ekspozycji rozpoczynał się w momencie odbudowania sieci przez pająka. Po ekspozycji sieci oczyszczano manualnie pęsetą z większych fragmentów zanieczyszczeń, np. liści, niewielkich owadów, a następnie szczelnie zamknięte transportowano w szalkach Petriego do laboratorium.

Jako drugi bioindykator wykorzystane zostały porosty - gatunek pustułka pęcherzykowata (*Hypogymnia physodes (L.)*). Metoda bioindykacji, w której jako organizmy biowskaźnikowe wykorzystuje się porosty (*Lichenes*) to lichenoindykacja. Metoda ta uznawana jest za jedną z najczulszych wśród metod bioindykacyjnych, pozwalającą badać zanieczyszczenia środowiska przede wszystkim dwutlenkiem siarki, a także tlenkami azotu, metalami czy radioaktywnymi izotopami. Procesy fizjologiczne porostów zależne są od wody atmosferycznej, przez co podstawowym warunkiem ich prawidłowego wzrostu jest jakość i stopień zanieczyszczenia tej wody. Możliwość wykorzystywania wody zawartej w powietrzu pozwoliła porostom uniezależnić się od podłoża i opanować różnorodne siedliska. Ze względu na taką fizjologię porosty wykazały reakcję na zwiększające się zanieczyszczenia atmosfery, m.in. tlenkami siarki, azotu oraz związkami ołowiu (Bystrek, 1997; Matwiejuk, 2014). Porosty charakteryzuje duża odporność na brak wody, na skrajnie niekorzystne temperatury czy krótki okres wegetacyjny, a jednocześnie cechuje je wyjątkowa wrażliwość na zanieczyszczenia atmosfery. Zwiększona czułość porostów związana jest z ich budową. Brak tkanki okrywającej oraz prowadzenie wymiany gazowej całą powierzchnią plechy, pozwala porostom na szybką absorpcję zanieczyszczeń gazowych, pyłowych oraz tych wnoszonych w formie jonowej z opadem. Co więcej, glony budujące porost mają niską tolerancję na zanieczyszczenia, która wynika z podatności chlorofilu na dezaktywację i braku tkanki okrywającej. Kolejnym czynnikiem wpływającym na zwiększoną wrażliwość porostów w porównaniu do innych roślin jest bezpośrednie pobieranie wody z opadów lub pary wodnej, bez uprzedniej filtracji tej wody przez glebę (tak jak w przypadku roślin). Równie duże znaczenie ma tu fakt, że zawartość chlorofilu w plechach porostów jest mniejsza niż u roślin, co po rozkładzie go przez toksyny daje efekt większego uszkodzenia plechy (Fałtynowicz, 1995; Matwiejuk, 2014). Powyższe czynniki wpływają na to, że porosty są chętnie wykorzystywane w bioindykacji, a analiza zarówno mikro- jak i makroelementów, skumulowanych w plechach porostów, pozwala wyznaczyć strefy zanieczyszczenia środowiska oraz wskazać potencjalne źródła zanieczyszczeń (Matwiejuk, 2014).

Na potrzeby niniejszej pracy badawczej porosty do transplantacji (o minimalnej początkowej zawartości metali) zebrane zostały w Stobrawskim Parku Krajobrazowym. Na jeden pakiet porostowy użyto około 5 gałązek z porostami, które związano razem sterylną żyłką. Tak przygotowane pakiety rozmieszczano w wybranych lokalizacjach na okres ekspozycji wynoszący ok. 2-3 miesiące. Pakiety porostowe zawieszane były na gałęziach drzew, na wysokości około 1,5 m, w lokalizacjach zgodnych z lokalizacją punktów pomiarowych z sieciami pajęczymi. Po zdefiniowanej ekspozycji w terenie pakiety porostowe były zbierane i szczelnie zamykane w torbach papierowych na czas ich transportu do laboratorium.

Oprócz wyżej wymienionych bioindykatorów do przeprowadzonych badań wykorzystany został również pyłomierz DIGITEL DHA 80 oraz analizator HORIBA PX-375. DHA 80 to wysokoobjętościowy pobornik pyłu zawieszonego firmy DIGITEL, służący do poboru PM_{10}, $PM_{2,5}$ oraz PM_1, czyli frakcji pyłu zawieszonego o średnicach mniejszych niż 10 μm, 2,5 μm oraz 1 μm odpowiednio. Urządzenie DIGITEL DHA 80 otrzymało certyfikat potwierdzający zgodność z normą PN-EN12341, dotyczącą wyznaczania stężeń masowych pyłu zawieszonego (PM_{10} lub $PM_{2,5}$) w powietrzu atmosferycznym poprzez pobieranie pyłu na filtry oraz określanie ich masy za pomocą wagi. Ważną zaletą jest to, że oprócz uzyskania informacji o stężeniu pyłu, umożliwia ono również fizyczny pobór próbek pyłu zawieszonego, który można następnie poddać analizom chemicznym. Do analiz z wykorzystaniem pyłomierza użyto filtrów kwarcowych QMA o średnicy 150 mm firmy Whatman.

Drugim z wykorzystywanych w badaniach urządzeń był analizator pyłu HORIBA PX-375. Pozwala on na automatyczny ciągły pomiar stężenia cząstek stałych za pomocą rozproszenia promieniowania beta oraz jednoczesny pomiar stężenia wybranych metali w pyle przy pomocy analizy rentgenowskiej (XRF). Pomiary wykonuje się są bezpośrednio w terenie, a wyniki dotyczące stężenia masowego pyłu zawieszonego (PM; z ang. particulate matter) oraz stężenia konkretnych pierwiastków w PM podawane są na bieżąco. Pozwala to na bardzo szybką identyfikację źródeł zanieczyszczenia powietrza.

Pomimo niezaprzeczalnych zalet specjalistycznego sprzętu opisanego powyżej, istnieje potrzeba używania tanich, łatwo dostępnych narzędzi, dzięki którym możliwe będzie analizowanie jakości powietrza w większej liczbie punktów pomiarowych, a koszt przeprowadzenia takiego badania będzie stosunkowo niski. Stąd też w tej dysertacji postanowiono skupić się na ocenie przydatności wykorzystania bioindykatorów do szacowania jakości powietrza. Jednakże, żeby informacja otrzymana z analizy danych zebranych z zastosowaniem bioindykatorów była wiarygodna konieczne było ich przetestowanie i sprawdzenie, czy informacja, jaką dostarczają jest zgodna z automatycznymi metodami referencyjnymi.

3.4. Omówienie zagadnień podnoszonych w publikacjach

Artykuł 1

Praca przeglądowa podsumowująca dotychczasowy stan wiedzy na temat wykorzystania sieci pajęczych w biomonitoringu zanieczyszczeń powietrza

The use of spider webs in the monitoring of air quality - a review. **Agnieszka Stojanowska**, Farhad Zeynalli, Magdalena Wróbel, Justyna Rybak. *Integrated Environmental Assessment and Management.* 2022, vol. 17, nr 1, s. 1-13.

Praca ta jest podsumowaniem stanu wiedzy na temat wykorzystania sieci pajęczych w biomonitoringu zanieczyszczeń powietrza. W niniejszym artykule przedstawione zostały trzy typowe procedury, stosowane podczas korzystania z tego nowego narzędzia, tj. transplantacja sieci pajęczej pozyskanej z laboratoryjnej hodowli pająków, pobór próbek *in situ* (ze znanym czasem ekspozycji na zanieczyszczenia) oraz pobór próbek *in situ* bez znanego czasu ekspozycji. Wśród nich, najlepsza okazuje się być pierwsza metoda, która zapewnia: (i) transplantowanie niezanieczyszczonej sieci pajęczej na dowolne stanowisko badawcze; (ii) odpowiednią ilość materiału do badań oraz (iii) ułatwia określanie czasu ekspozycji na zanieczyszczenia. Duża część tej pracy poświęcona została opisowi gatunków pająków, wykorzystywanych w tego typu eksperymentach. Jest to o tyle ważne, że różne gatunki pająków budują różne typy sieci pajęczych, co z kolei może sprzyjać lub utrudniać akumulację stałych cząstek zanieczyszczeń powietrza. Jako najlepsze uznaje się pająki z rodziny Agelenidae, które nie mają nawyku zjadania swoich sieci, dzięki czemu pobór próbek w terenie, jak i hodowla laboratoryjna pająków, w celu pozyskania czystej sieci są możliwe. Specyficzne ułożenie nitek sieci sprzyja akumulacji na nich zanieczyszczeń atmosferycznych. Co więcej, ich konstrukcje mogą osiągać pokaźne rozmiary, co z kolei ułatwia zebranie odpowiedniej ilości materiału do dalszych analiz chemicznych. W pracy omówiony został także optymalny czas ekspozycji próbek na zanieczyszczenia, który zazwyczaj wynosi około 60 dni, ale jak pokazują analizowane prace jest on zależny od rodzaju i miejsca przeprowadzanego eksperymentu. Przeglądowa praca zawiera również rozdział dotyczący oceny metod analitycznych wykorzystywanych do badania cząstek pyłowych zakumulowanych na sieciach pajęczych. Wyróżnia się metody prowadzące do ilościowej oraz jakościowej oceny zanieczyszczeń, a wybór odpowiedniej metody zależy od celu i zakresu przeprowadzanych badań. W pracy podkreślony zostaje niski koszt badań przeprowadzanych z wykorzystaniem sieci pajęczych, który jest dużo bardziej atrakcyjny ekonomicznie niż w przypadku standardowo stosowanych metod monitoringowych.

W końcowej części artykułu przedstawione zostało porównanie biomonitoringu z wykorzystaniem sieci pajęczych z innymi powszechnie wykorzystywanymi bioindykatorami. Udowodniono, że to nowe narzędzie biomonitoringowe może zostać uznane za dużo bardziej przydatne. Jest to związane m.in. z nieograniczoną sezonowo możliwością pozyskiwania sieci do badań, czy możliwością prowadzenia eksperymentów również w środowiskach bardzo zanieczyszczonych.

Artykuł, oprócz podsumowania obecnych badań, wskazuje również braki w aktualnym stanie wiedzy oraz przewiduje możliwe ścieżki rozwoju metody i perspektywy na kolejne eksperymenty. Mocno podkreślono fakt, że aby móc w pełni korzystać z metody sieci pajęczych w biomonitoringu powietrza należałoby sprawdzić, czy wyniki z pajęczyn mają związek z wynikami uzyskanymi dzięki prowadzeniu standardowego monitoringu jakości powietrza na danym obszarze.

Wniosek: Sieci pajęcze mają potencjał jako bioindykator przy ocenie jakości powietrza, jednak istnieją luki w wiedzy, stąd potrzeba prac, które by te niejasności wyjaśniły.

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Critical Review

The use of spider webs in the monitoring of air quality—A review

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Abstract

Methods for using spider webs as passive air samplers have been developed over recent years and reported in more than a dozen articles. In this article, we present the typical procedures followed when using this new tool and critically review its application in air pollution assessment. To understand the state of research and application of spider webs in this field, we describe some advantages and disadvantages of their use in the analyses of air contaminants. The aim is to summarize the current knowledge on this subject, highlight gaps in the present studies, and arouse the interest of scientists on this issue. The increased effort could result in the standardization of the method at the national and international level. *Integr Environ Assess Manag* 2022;00:1–13. © 2021 SETAC

KEYWORDS: Air quality, Bioindicators, Biomonitoring, Pollution, Spider webs

INTRODUCTION

Air pollution is a growing concern worldwide and represents the greatest environmental risk to health (World Health Organization, 2016). Airborne particulate matter (PM) is now a major problem in Europe (European Environment Agency, 2019) and causes respiratory diseases leading to premature death (World Health Organization, 2013). Airborne particles can be distinguished by their size and categorized accordingly as PM_{10}, $PM_{2.5}$, and $PM_{0.1}$ (World Health Organization, 2002), where the subscript reflects the maximum particle size in micrometre (μm). Of these, the smallest particles are the most dangerous (Hsu et al., 2016). Whereas coarse particles are stopped in the laryngeal and nasal area (Martonen et al., 2002), ultrafine particles can enter the lungs, become absorbed into the bloodstream, and accumulate in organs (Oberdörster et al., 2004; Takenaka et al., 2001). Because of the pivotal role that air quality plays in the well-being of living organisms, it should be constantly monitored, and air pollution must be kept within the regulatory limits. To fulfill these requirements, specific equipment is needed. However, practical constraints, such as high cost, need for continuous supervision, and limitations related to the location of monitoring points (i.e., mountainous or woody areas), limit the use of such equipment. Therefore, alternative or complementary ways of assessing air quality are required, and biomonitoring, which relies on the use of living organisms or their products, is one of them. Lichens, mosses, and tree leaves are commonly and widely applied; however, a new type of bioindicator (i.e., spider webs) has emerged and is becoming more popular (Figure 1).

Spider webs are made of silk, which is protein-based and produced by the spinnerets that are located on the abdomen. Originally, spider silk was probably only used to protect the eggs. The hunting properties of spider webs are a much later evolutionary invention. The unique features of the webs, which allow the capture of prey, facilitate their use for air pollution monitoring because the particles of dust can be trapped on the web as prey is trapped. The first article that considered the application of webs for biomonitoring was presented in 1990 by James et al. (1990). The study was conducted in the Jenolan Caves (Australia). It was proposed that the pollutants (in particular, lead, produced by cars) may contribute to this situation. Hose et al. (2002) developed the idea and stated that "spider webs provide a useful indicator of environmental pollution and chemistry." Since then, spider webs as bioindicators are becoming increasingly popular. Spider webs have many advantages because they are inexpensive, organic, easy to find, and, unlike most passive samplers, they are nonselective and can accumulate diverse types of pollutants (i.e., potentially toxic elements [PTEs], polycyclic aromatic hydrocarbons [PAHs], dioxins). Additionally, the product is natural, meaning that the production of additional waste (i.e., used filters) can be avoided. The efficient accumulation of pollutants allows them to be used for long-term monitoring, usually 2–3 months, which is the optimal period in terms of obtained results (Rutkowski, Jadczyk, et al., 2018).

Spider webs are characterized by high elasticity, remarkable strength, and unusual toughness (Gosline et al.,

This article includes online-only Supporting Information.

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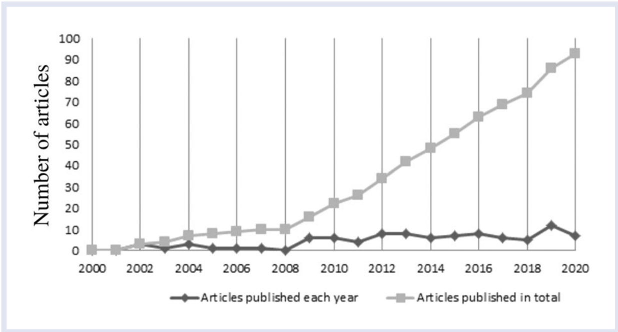

FIGURE 1 The number of articles published in PubMed-indexed scientific journals that contained the phrase "spider webs" both in their titles and abstracts from 2000 to 2020 (PubMed Advanced Search)

1999; Swanson et al., 2009). As a result, webs are the focus of intensive research to better understand their properties. For this review, we have chosen 19 studies concerning the use of spider webs in biomonitoring. More than half of the articles chosen were conducted in Poland; the rest are from Australia (10.5%), Pakistan (10.5%), Nigeria (10.5%), Germany (5.3%), China (5.3%), and India (5.3%). Therefore, the idea of spider webs as biomonitors is still not widespread and is used in only a few countries, although it is continuously developing and expanding.

STUDIES OF SPIDER WEBS

Diversification of methodology

For the assessment of air pollution, it is common to use webs made by spiders that do not routinely eat their webs, such as representatives of the Araneidae that eat their old web and reconstruct a new web daily or if damaged. Such turnover of web material could influence the results of studies. Three approaches to using spider webs as biomonitors have been developed:

1. Transplantation: common in studies where quantitative analysis is needed and when the exact concentration of pollutants collected on webs must be provided in a defined period. For transplantation, a clean spider web is produced by laboratory-bred spiders and is then manually stretched over a Petri dish. Webs can then be brought to the study area and left there for exposure (Stojanowska et al., 2020). Górka et al. (2018) confirmed that the process of collection of atmospheric particles on spider webs in laboratory conditions is negligible. This method has been used in four studies.
2. Collection of spider webs in situ with unknown exposure time: commonly used in qualitative studies. This method has been used in four studies.
3. Collection of spider webs in situ with known exposure time: consists of destroying the old web and observing the sampling point for the creation of the new web. This method is often used but requires the daily monitoring of the sampling point. This method is the most commonly used, and it was studied 14 times.

Although the third method is actually the most commonly used, the first method seems to be the best option because daily observation of different sampling points is not required, the exposure time can be defined easily, and it is certain that the newly created spider web has not been contaminated in the process of its creation. However, a drawback is the need to have a person to take care of the spiders. Another issue is the preparation of samples for further outdoor and/or indoor use. In general, two approaches have been applied. The first one, the method of Champion de Crespigny et al. (2001), can be used to prepare the spider webs for field deployment. Standard sized wooden frames are first settled by spiders in the laboratory, which then weave webs on those frames that can be deployed in the field. The second approach is based on the already woven webs, but they are stretched manually on Petri dishes and then transferred to the study sites (Stojanowska et al., 2020).

The last problem concerns the details of how to control environmental factors (e.g., wind, rain, snow) when using spider webs and the selection of study control areas. To protect sample points from heavy rain or snowfall, secluded locations for spider webs are usually chosen such as tunnels or bridges (e.g., Rybak & Olejniczak, 2014). Furthermore, spiders can be protected by additional built shelter. If the presence of spiders is noticed in these sites, they are visited daily and observed. Additionally, the Stojanowska et al. (2020) method is recommended because it is based on the use of already woven webs, stretched over Petri dishes and fixed with hot glue at appropriate, protected sampling sites and left to be exposed to pollutants, with suitable protection against severe weather conditions.

Species used in biomonitoring

We noted diversity in the spider species whose webs were used for bioindication studies (Figure 2). Some articles (Ayedun et al., 2013; Riaz et al., 2014) provided no information about the spider species or stated only the spider families (Tahir et al., 2018; van Laaten et al., 2020), which accounts for 21.05% of all analyzed articles. On the other hand, the webs of *Eratigena atrica* were used in approximately 30% of the articles, which makes this species the most commonly used in air pollution biomonitoring.

Eratigena atrica, also known as the giant house spider, belongs to the family Agelenidae (funnel-web spiders). It is native to Europe (Bolzern et al., 2013) and is an introduced species to Northern America (Crawford & Vest, 1989). The webs of *E. atrica*'s could be found indoors (on floor or walls) and outdoors (logs and under rocks). Unlike orb webs, webs of *E. atrica* and other agelenids are a nonsticky, dense sheet (Nyffeler et al., 1994), which enhances the ability to catch airborne particles. This makes them very suitable for such studies, especially in Poland where *E. atrica* is common. The additional advantage is that this species can be active year-round; therefore, it can be applied regardless of the season.

Other commonly used species were *Tegenaria ferruginea*, *Agelena labyrinthica*, *Tegenaria silvestris*, and *Eratigena*

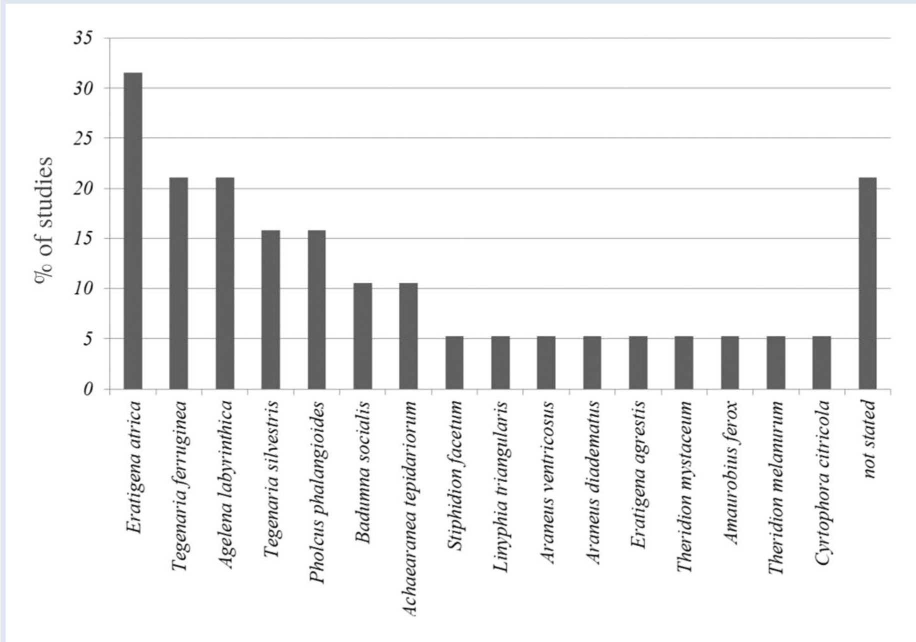

FIGURE 2 List of 16 spider species used in 19 analyzed biomonitoring studies

agrestis, which also belong to the Agelenidae family. The web type is the same for all family members (Roberts, 1995). Most Agelenids occur in dark, abandoned places such as tunnels or under bridges, and they are present year-round even in low temperatures (Roberts, 1995).

Other families used in air pollution studies were Pholcidae (*Pholcus phalangioides*), Desidae (*Badumna socialis*), Theridiidae (*Achaearanea tepidariorum*, *Theridion mystaceum*, *Theridion melanurum*), Stiphidiidae (*Stiphidion facetum*), Linyphiidae (*Linyphia triangularis*), Araneidae (*Araneus ventricosus*, *Araneus diadematus*, *Cyrtophora citricola*), and Amaurobiidae (*Amaurobius ferox*).

Agelenidae, Stiphidiidae, Desidae, and Amaurobiidae are cribellate families or contain at least some cribellate spiders and are closely related because they belong to the Amaurobioid superfamily (Ubick et al., 2005). Cribellate spiders have a spinning plate (cribellum) in front of the spinnerets that distinguishes them from ecribellate spiders that do not have a cribellum. It consists of plates with numerous minute spigots producing very fine fibers. Cribellate spiders produce nanofibers as their capture threads. Spiders with a cribellum also have a comb (calamistrum), on the metatarsus of the spider's fourth legs, which can produce characteristic woolly silk. The structure of fibers is so tiny that it gives strong adhesion of prey without any glue (Bott et al., 2017), although the web structure differs among these four cribellate spider families. Ecribellate without such a cribellum have capture threads consisting of two core fibers out of flagelliform silk and glue droplets to capture prey. Therefore, they rely mainly on glue-like silk to capture prey (Vollrath, 1992).

All four cribellate families have proven their usefulness in bioindication. Desidae and Amaurobiidae have woolly "lace webs" that can occur in houses and their surroundings. Stiphidiidae and Agelenidae produce funnel-like webs (Foelix, 2011; Hose et al., 2002; Xiao-li et al., 2006). It is probably no coincidence that these families are the most popular choice in bioindication research because of the unique (dense) properties of the webs, which suggests that other closely related families such as Amphinectidae may also be suitable for this type of research.

Pholcidae are ecribellate spiders, and they are abundant in urban areas. They are very common in houses because Pholcidae are mostly synanthropic species. They weave very irregular webs usually in wall corners, basements, and parking areas. Their webs are loose, large, irregular, but nonsticky, and they are commonly found in dark places. In warmer countries, the cycle of reproduction and development takes place year-round; however, in Poland, this spider is active all year in households only. Because their nets are woven in places that are rarely cleaned, when the web becomes dirty, the spider leaves it and finds another place to construct a new one (Roberts, 1995). In addition to all these advantages, their webs are characterized by a coarse mesh that could be considered a drawback in the process of capturing airborne particles.

The webs of cribellate Amaurobiidae do not contain glue, but are made of tangled, dry, electrostatically charged silk, which consists of clouds of nanofibers that enhance the capture of prey (Foelix, 2011; Joel et al., 2015). Amaurobiid spiders are usually found in walls, caves, or tunnels, but they are normally active only in spring and early summer (Foelix, 1996). Additionally, the collection of samples can be complicated because webs are woven close to the walls.

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Further, in late autumn, the spiders tend to hide inside houses, which is a disadvantage for their broader use.

Theridiidae, ecribellate spiders, occur in urban areas, on house walls, and in road tunnels. Their webs have the structure of a loose, irregular, nonsticky, three-dimensional tangled sheet, suspended on vertical threads forming a scaffolding. It is additionally tensioned with mooring threads running diagonally to the ground (Foelix, 2011). Some Theridiidae build shelters within the web (e.g., *A. saxatile*) and construct silk tubes hanging vertically in the center of the web. The spider camouflages the hiding place with plant fragments and grains of earth. The South African *Achaearanea globispira*, in turn, makes spiral shelters. A spider web is hung on the thread, and several glue-covered trap threads extend from the bottom of this species' refuge to the ground (Henschel & Jocquet, 1994). However, their webs are very small, which can be a great disadvantage for studies.

Linyphiidae, belonging to ecribellate spiders, are the second most widespread spider family in the world (Samiayyan, 2014). Despite their abundance, their webs have been used in only one bioindication study so far to measure magnetic susceptibility (MS; Rachwał et al., 2018). Most linyphiids weave sheet-like or cup-shaped, nonsticky webs, which consist of irregular vertical layers.

Desidae are a small cribellate family, known mostly from Australasia and some species from South America (World Spider Catalog, 2022). The webs of *B. socialis*, which belongs to the Desidae family, were used in two studies. These spiders can be found over rocky areas and crevices and create nonsticky webs made of cribellate silk with funnel openings. In general, spiders belonging to the *Badumna* genus have only been recorded in Australia, New Zealand, and Papua New Guinea. Therefore, even if their webs are nonsticky, the small size of the family and their limited spread may be a disadvantage and exclude them from common use. The Stiphiidae family, with the limited occurrence, have a similar problem. Most species of this family can be found in Australia and New Zealand, although only *S. facetum* was used for bioindication studies. It creates its webs on rocky areas, trees, or near buildings; their very thickly woven nonsticky sheets are made of cribellate silk and hang like a hammock, attached to the substrate by supporting threads at several points around the circumference (Hose et al., 2002; Marples, 1959). However, their limited spread excludes them from common use.

Spiders from the ecribellate Araneidae family, the third most widespread spider family in the world, weave orb webs (Samiayyan, 2014). The web consists of a stressed flat sheet created by irregularly arranged dense threads (Rachwał et al., 2018). This type of web has three components: (1) radial threads converging in the center, (2) frame threads that represent the attachment and place of attachment, and (3) spiral. Orb-weaving spiders (Araneidae) spin their webs at nightfall and take them down and eat their webs usually 1 h before dawn (Stowe & Lane, 1978). Their webs are sticky, and a disadvantage of sticky webs is that they contain glue droplets (Sahni et al., 2010), which may attract various artifacts that might hinder the analysis, whereas such a problem does not exist in nonsticky webs. Additionally, the habit of eating its own web is also considered a disadvantage.

The question of the properties and structure of the web in the context of its suitability for bioindication is still open. The circular ecribelletae and cribellatae webs are remarkably similar in their overall construction plan, with the only differences being in their spatial arrangement (vertical or horizontal) and the type of building material used. There can be distinguished prey capturing webs that are built of nonsticky ampullate silk structural elements with the addition of some sticky threads that catch prey. In most orb webs and cobwebs, these capture threads are covered with specific glue droplets, which makes the silk viscous (Blackledge, 2012). Generally, typical orb webs are not very suitable for such research for two reasons: the presence of large empty spaces in the webs, which greatly influence the size of the sample, and the habit of those spiders eating a damaged web. On the other hand, cribellate threads are covered with many dry nanofibers that also generate and enhance adhesion (Joel et al., 2015). If cribellate webs that lack “glue” present different opportunities over webs that have glue, which is better? The glue does not necessarily retain the contaminants inside the webs, which depends on the type of contamination and on the nature of the webs themselves. As discussed above, the dense structure itself is able to retain the pollutants; furthermore, webs are probably more suitable for the indication of organic compounds such as PAHs or other organic species due to their chemical affinity, which helps them penetrate webs more deeply and bind to the webs' protein matrix (absorption), as suggested by Rybak and Olejniczak (2014). This could make it difficult to extract PAHs and other organic species from the web. Spider silk is a biopolymer (fibroin), which could exhibit intermolecular interaction with some organic compounds emitted during the combustion of fuel. On the other hand, some compounds probably do not bind to the web structure and can easily be washed off by rain or even wind.

To summarize, the family of Agelenidae seems best suited for biomonitoring because they occur widely (1342 species in 90 genera; World Spider Catalog, 2022) and are active even at low temperatures, they do not eat their own web, and the webs are large and dense. The location of web construction is also favorable and allows studies to be carried out in situ. What is more, the ease of maintaining laboratory-bred spiders makes it feasible to perform translocation studies. Other representatives, especially from the Pholcidae and Theridiidae families, are not very abundant. Theridiidae webs are often small and difficult to access, although the weaving itself is dense and favors the deposition of pollutants. Pholcidae webs, on the other hand, are irregular, often composed of several threads crossed with each other, which are mechanically broken very quickly. This is also the case for Aranaeidae as their webs are regular but have many empty spaces, which makes it difficult to use them for sample collection. Although the use of Linyphiidae webs is definitely noteworthy, their structure is suitable for capturing pollutants as demonstrated by Rachwał et al. (2018).

Exposure time

The exposure time of spider webs to pollutants varies among studies and usually ranges from five or seven days (Ayedun et al., 2013; Bhati et al., 2018; Xiao-li et al., 2006; Yalwa & Kabo, 2015) to 24 months (Rachwał et al., 2018). However, the most common sampling lasted 60 days (Rutkowski et al., 2019; Rybak, 2014, 2015; Rybak & Olejniczak, 2014;
Stojanowska et al., 2020). The length of exposure depends on the level of contamination of the study area, that is, if the contamination is high then the exposure time might be shorter.

Cost analysis of the use of spiders versus conventional monitors

As mentioned above, biomonitoring with spider webs can have minimal cost, but depends on which technique is used. For in situ sampling, the web can be collected with a glass stick and stored in a glass vial (for chemical analysis); however, for a scanning electron microscopy with energy dispersive X-ray analysis (SEM-EDX), it is important not to entangle the web, so it must be collected in stretched form on the petri dish. Another issue is when the transplantation method is chosen for the studies. In this situation, more work is needed because spider breeding must be constantly maintained. For this purpose, the cost will be higher at the beginning of the experiment because terraria for spiders must be established. Then, at least once or twice a week, the spiders must be fed with *Drosophila hydei* and/or *Tenebrio molitor* larvae (for larger spiders). They must be purchased at the beginning of the experiment, and then they can be easily reproduced in the laboratory. The collection of uncontaminated webs is normally done with the use of Petri dishes on which the spider web is stretched (Stojanowska et al., 2020). The cost of the spider web analysis, after the exposure, is a different issue, not discussed in this study, but general methods used for this purpose are mentioned below.

Generally, in passive air pollution monitoring, diffusion tubes are commonly used, which are considered cost effective. They usually provide the information about average pollution concentrations and, due to the low cost, they are frequently used in the studies indicating the hot spots, especially along roads. Another advantage is that the tubes are simple to use and require no specialized training. However, the tubes are suitable for only a few specific pollutants (e.g., NO_2, SO_2, benzene, toluene, and xylene; https://airquality.gov.wales/about-air-quality/monitoring/monitoring-methodologies).

Low-cost sensor systems are also used in passive air quality monitoring. They are characterized by their small size, low power demand, and prices starting from a few hundred British pounds (for one pollutant). Despite the price, they are still considered cost effective because they can provide very highly time-resolved data (https://airquality.gov.wales/about-air-quality/monitoring/monitoring-methodologies).

Conventional passive samplers are rather inexpensive, unobtrusive, and do not require electrical power. In addition to the concentration of collected particles, some passive samplers can also provide information about the particle size distribution (Leith et al., 2007).

Analysis of spider web

There are two different ways of analyzing spider webs after exposure in the field. The pollution collected on threads can be analyzed qualitatively or quantitatively. The quantitative information of elements on the web can be obtained by flame atomic absorption spectrometry as done by Stojanowska et al. (2020) and Xiao-li et al. (2006), inductively coupled plasma mass spectrometry as presented by Bartz et al. (2021), or inductively coupled plasma optical emission spectrometry as in Rybak (2015). On the other hand, SEM-EDX provides qualitative information about particle size, form, and mineralogical composition (Bartz et al., 2021; Górka et al., 2018). For PAHs, analysis by gas chromatography is used (Rybak, 2014; Rybak & Olejniczak, 2014).

POLLUTANTS IDENTIFIED ON WEBS AND LIMITATIONS OF STUDIES

PTEs and other elements

Potentially toxic elements (PTEs) are of great concern because many are emitted into the atmosphere by anthropogenic sources and are dangerous to human health. Moreover, such pollutants with dust can be transported easily by air movement, and they can reach areas located far away (Bartz et al., 2021). Particulate matter with PTEs can settle down by dry or wet deposition and accumulate on passive samplers (i.e., spider webs). One of the first articles to assess air pollution in a defined area and analyze the two elements in the webs of two species, *B. socialis* and *S. facetum*, was by Hose et al. (2002). It was mentioned that the relationship between the pollutants in the air and those measured in webs should be studied in future research. As yet, however, only two studies have attempted to compare the pollution collected on the web with the actual air pollution (Rybak et al., 2015; Stojanowska et al., 2021). However, due to different mechanisms of particle accumulation (mechanically controlled flow versus sedimentation) and differentiation in the size of accumulated particles, the comparison was difficult. This issue needs further development because it is crucial for air pollution biomonitoring.

Motor vehicle emissions are considered a major source of airborne particulates in urban areas (Gertler et al., 2000). So, many articles consider this issue and track motor vehicle emissions. For example, Xiao-li et al. (2006) used spider webs to analyze the air pollution (Pb, Zn, Cu, and Cd) in urban sites in China and demonstrated that this passive sampler is an effective indicator of metal pollution produced by motor vehicle traffic. Further, a distance-dependent decrease in metal concentrations was recorded. The variation of metal concentrations (Pb, Cd, Zn, Ni, Cu) at different distances from the road was also studied by Ayedun et al. (2013). The concentrations of Pb at the distance of 100, 200, and 300 m from the road were 0.34, 0.18, and 0.09 $\mu g\,g^{-1}$, respectively. This demonstrated that the proximity of the sample site to a busy road is crucial to measuring Pb concentrations. Another example is the article by Rybak (2015), which was the first article where the author tried to assess small-scale distribution of airborne major and trace elements with the use of spider webs. The elements, accumulated on webs (V, Mn, Ni, Cu, and Pb), were correlated with the emissions from motor vehicles.

The selection of the elements in studies is based mostly on dominant pollutants in the study area. Thus, many studies focus mostly on very contaminated places such as industrial or urban areas (Figure 3). Because spiders weave their webs everywhere (i.e., in natural and very contaminated sites), they can be used successfully to trace the pollution produced by motor emissions and smelters.

An overview of 12 studies of PTEs concentrations on webs reveals that the most commonly analyzed element is lead. Lead is the most prominent PTE, together with zinc, resulting from automotive emissions (Xu et al., 2014). Other elements studied are copper (in seven studies), nickel (six studies), cadmium (four studies), iron, manganese, and chromium (each in three studies), and other elements such as Ti, Mo, Pt, and W (in only one study).

Size of collected particles

Size of collected particles may differ depending on the main source of the pollution in a given area. However, according to studies conducted by Bartz et al. (2021), the fraction <2.5 μm dominates, while the fraction >10 μm is the least abundant. This is particularly important because PTEs caused by anthropogenic activities are associated mostly with the smaller fractions (Hueglin et al., 2005), although natural ones, connected with the erosion of the Earth's crust, occur normally in larger size fraction (Chtioui et al., 2019). Górka et al. (2018) reported that the size of collected particles also depends on the spider species and the construction of their web. The study focused on two different species, both building nonsticky webs. The difference is that the webs of *E. atrica* (Agelenidae) are constructed of thin, rounded threads, and the web is in the form of a sheet, although the web of *P. phalangioides* (Pholcidae) is three-dimensional, large and loose, and built of thicker threads with irregular diameters. Surprisingly, the web of *P. phalangioides* had better adsorption of smaller particles, which may be connected with the specific characteristic of the single thread. Furthermore, the results demonstrated that during 40 days of exposure, 92%–97% of the collected particles were smaller than 10 μm (Górka et al., 2018). However, in the web exposed for two years, approximately 20% of collected particles ranged in size from 10 to 100 μm, which may indicate that some particles can form aggregates during long exposures. Another explanation can be the supposition that larger fractions (>10 μm) may need more time to settle and accumulate on the web (Górka et al., 2018).

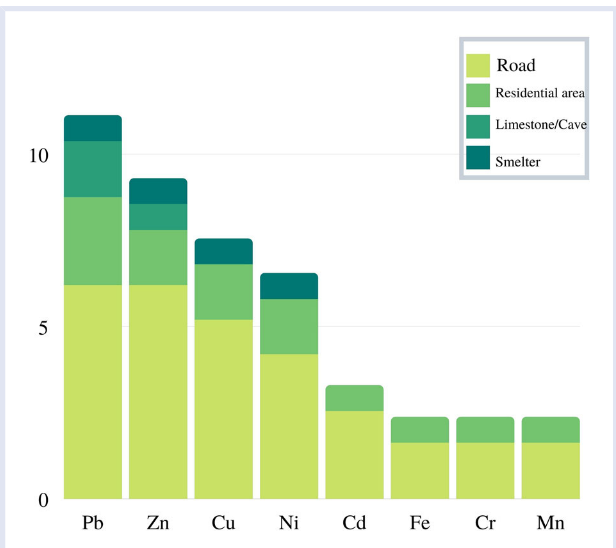

FIGURE 3 The most prominent, potentially toxic elements found in spider webs and their areas of study (according to the studies listed in Table S1)

Limitations of studies of elemental analysis

The adsorption of metals in webs can be connected with the following mechanisms: (i) entrapment of particles that contain metals adhering to the web and (ii) consumption of polluted prey insects by the spider and accumulation of pollution inside the threads of spider webs. However, research has rarely focused on these two mechanisms and, thus, our understanding is limited. Hose et al. (2002) found that metals (Pb, Zn) settle on the web surface and are not incorporated into the web matrix (the first mechanism). They analyzed cribellate spiders (*B. socialis* and *S. facetum*) and found that washing the webs with diluted acid reduced metal concentrations up to 80%. These types of webs do not have sticky glue and rely on the dense network of silk fibrils, which is extremely effective in trapping particulate contaminants. Apart from Hose et al. (2002), the mechanism of trapping air contaminants by spider webs has been studied twice (Rybak, Rogula-Kozłowska, Loska, et al., 2019; Wilczek et al., 2017), but in these cases the studies suggested that webs were made by the "polluted" spiders (the second mechanism). Wilczek et al. (2017) focused on assessing whether cadmium ingested by *Steatoda grossa* (cobweb spider; Theridiidae) influences the energy content and structural properties of the produced hunting web. Male spiders had higher body concentrations of metals than females. However, a change in their calorific values and structural features was not significant. In addition, Rybak, Rogula-Kozłowska, Loska, et al. (2019) found that the concentrations of Cu and Pb were higher in the bodies and webs of males than of females. There was also a positive correlation between the levels of Cu and Pb in webs and spider bodies.

Mechanisms of particle accumulation have been studied only a few times and need further investigation as they are not well understood yet. In addition, apart from the webs produced by the spiders mentioned above, the properties of other web types (i.e., spiral orb webs, tangle webs, or tubular webs) have never been analyzed, and are likely to differ in their effectiveness in trapping.

PAHs

Polycyclic aromatic hydrocarbons (PAHs) are prevalent in ambient air. Some are the deadliest known carcinogens, and most of them are produced by anthropogenic emissions (Ravindra et al., 2008). There have been only four studies related to the accumulation of PAHs on spider webs (Rutkowski et al., 2019; Rybak, 2014; Rybak & Olejniczak, 2014; Rybak, Rogula-Kozłowska, Jureczko, et al., 2019; summarized in Table S1). In general, samples from areas close to heavy vehicle traffic had higher mean concentrations of PAHs when compared with background sites (Rybak, 2014; Rybak & Olejniczak, 2014). Rybak (2014) revealed that the PAH concentration in the points located close to the road were significantly different from others, indicating the decrease in PAHs with increasing distance from the road. Thus, the use of spider webs in assessing the contamination with PAHs was proven. The studies mentioned above focused on assessing the PAH levels on webs in viaducts, roadway tunnels, and parking garages. In all these places, the specific air circulation exists, which enhances the longevity of gases and dust particles in those areas (Rogula-Kozłowska et al., 2008; Sternbeck et al., 2002). Additionally, spiders instinctively choose secluded places to build their webs (i.e., tunnels, which protect the webs from the rain and wind) and therefore, the accumulated pollutants can persist for longer. Tunnels and parking garages are also characterized by shading, which is an advantage because PAHs break down readily in sunlight. Conclusions from these studies suggest that spider webs are good indicators of PAH pollution because they simultaneously collect PAHs in gaseous and particulate form (Rybak, Rogula-Kozłowska, Jureczko, et al., 2019). Given the low cost of collecting web samples, they can be abundantly and widely distributed in the study area, which can be helpful because the volatility of PAH compounds differs. Further, the studies of PAHs with the use of webs can be conducted outdoors and indoors.

Limitations of studies of PAHs on webs

The dispersion and behavior of PAH compounds can depend on environmental conditions, although their chemical and physical properties play the main role. We can distinguish PAHs of high volatility (lower molecular weight) and low volatility (higher molecular weight). Particulate-adsorbed PAHs with low volatility are normally deposited close to the emission source, although PAHs with high volatility can be transported far away (Harmens et al., 2013). Therefore, special attention must be paid while analyzing the accumulated PAHs on spider webs. Rybak and Olejniczak (2014) found that only compounds with high molecular weight could be effectively trapped and assessed with webs while assessing the outdoor air quality. This suggests that more volatile, lighter molecular weight compounds are lost during or after sampling. To minimize this problem, the authors suggest applying spiders in restricted and closed polluted areas such as tunnels and car parks. What is interesting, when we compare studies of indoor with outdoor PAHs levels, we found that spider webs tend to bind most PAHs indoors (Rybak, Rogula-Kozłowska, Jureczko, et al., 2019), whereas during outdoor studies, only selected PAHs compounds could be trapped on spider webs (Rybak & Olejniczak, 2014). This is the result of quick outdoor photodegradation and microbial decomposition of some organic compounds. None of the authors studied if correlations exist among PAH concentrations in webs and dust samples. The mechanism of accumulation of organic pollutants has not yet been studied, although webs are probably more suitable for the indication of organic compounds such as PAHs or other organic species due to their chemical affinity, which helps them penetrate webs more deeply and bind to the protein matrix of the web (absorption).

OTHER STUDIES USING SPIDER WEBS

Magnetic susceptibility

The studies reveal that pollution levels caused by urban and industrial wastes containing metals can be detected by MS measurements (Jordanova et al., 2012). Many environmental materials (such as soil, dust, and living organisms, i.e., plants, lichens, mosses) reveal enhanced magnetic signals.

Just a few articles tried to assess the usefulness of spider webs in this field. First, Rachwał et al. (2018) studied MS in webs sampled from indoors and outdoors. Newly constructed webs were exposed usually for approximately 3–4 months for indoor samples and approximately one month for outdoor ones. Results proved that spider webs can be used as a proxy for studies of anthropogenically derived pollution. However, a positive relationship between the duration of web exposure and the MS was not observed. This could be connected with the fact that, for most of the samples, the exposure times were similar, and so the differences could not be noted.

In research by Rutkowski et al. (2020), magnetic susceptibility of urban road dust, settled indoors and outdoors on filters, was studied and compared with the data obtained with the use of spider webs. Magnetic measurements revealed elevated levels of magnetic pollutants at all sites studied. The indoor/outdoor ratios of magnetic susceptibility for the investigated matrices were comparable, which suggests that spider webs are a good tool for magnetic monitoring.

Limitations

In such studies, if the webs were taken from different spider families, the mass-specific magnetic susceptibility—which relies only on the sample masses—can be considered.

Because spiders can build two- and three-dimensional webs, it is impossible to measure the surface of the web exposed to pollution accumulation in the same standardized way (Rachwał et al., 2018). Moreover, differences in web structure make it impossible to determine the exact volume of the sample. However, depending on the purpose of the given study, it is sufficient to use a uniform, assumed volume (Rachwał et al., 2018).

Genotoxic and mutagenic studies (Ames test)

The mutagenic potential of chemical compounds is crucial to recognizing the real harmfulness of air pollution. Currently, for this purpose, the test proposed by Ames (Ames, 1971; Ames, Durston, et al., 1973; Ames, Lee, et al., 1973; Ames et al., 1975) is commonly used (e.g., Champion et al., 2020; Elassouli et al., 2007; Rutkowski et al., 2019). It is a rapid and reliable bacterial assay performed to evaluate a chemical's potential genotoxicity by measuring its ability to provoke reverse mutations of selected bacterial strains. In 2018 and 2019, spider webs were used for the assessment of air pollution mutagenicity using the Ames MPF test (Rutkowski, Jadczyk, et al., 2018; Rutkowski et al., 2019). In these studies, the mutagenicity of web samples collected outdoors and indoors was analyzed. According to previous researchers, the main pollutants of indoor air are nitrogen dioxide, tobacco smoke, carbon monoxide, biological agents, woodsmoke, and volatile organic compounds (after Rutkowski et al., 2019). So, the microplate Ames assay combined with the application of spider webs was found to be a promising tool for mutagenic studies of airborne particulates. It is important that the studies of indoor mutagenicity on spider webs are particularly encouraging because pollutants present in dust deposited on spider webs demonstrate that the indoor environment should be monitored more frequently. Such monitoring is simpler, easier, and less expensive with spider webs.

Studies of indoor and outdoor pollution with spider webs

Studies using spider webs have been performed mostly outdoors (most of the above-mentioned articles). However, a few articles (Rachwał et al., 2018; Rutkowski et al., 2020; Rybak, Rogula-Kozłowska, Jureczko, et al., 2019) demonstrated that using spider webs for evaluating indoor air pollution might be feasible. Given that people spend approximately 80%–90% of their time indoors (ASHRAE, 2011), monitoring indoor air quality is critically important, and inexpensive, simple, and reliable methods for monitoring air quality are needed. Unfortunately, as for now, the application of advanced professional equipment to monitor air quality at every household is not possible because it requires constant supervision and can be very expensive. On the contrary, webs are present in almost every house; therefore, the information on possible pollutants in our habitats can be easily available.

For outdoor studies, it is very important to properly plan the location of the samples, protecting them from strong wind or rain. On the other hand, in indoor studies, such problems do not exist because the webs are sheltered from weather conditions. Moreover, in indoor studies, there is a smaller possibility that the samples could be destroyed by human beings or animals.

Limitations

For the application of spider webs in such studies, standardization under laboratory conditions is required. The problem is related to the lack of norms and procedures for indoor air quality control, which, as a result, gives diversifications of studies. This means that previous studies have used a variety of sampling methods and analytical equipment, which complicates the comparison of results.

COMPARISON WITH OTHER BIOINDICATORS—ADVANTAGES AND DISADVANTAGES

Spider webs accumulate PM similar to other flora-based indicators (e.g., mosses, lichens, tree leaves; Rachwał et al., 2018). However, the accumulation of pollution in a spider web is greater when compared with lichens or mosses (Stojanowska et al., 2020; van Laaten et al., 2020). These findings need further study to better understand such phenomena. Further, the application of other types of bioindicators is limited due to the duration of the vegetative season and the lack of sunlight, which preclude them from use in tunnel or parking garages.

Lichens are one of the most commonly used bioindicators of air pollution, which is proved by the number of studies devoted to them (Adamo et al., 2003; żCiężka et al., 2016; Kłos et al., 2018; Stojanowska et al., 2020). This is because their uptake depends strictly on atmospheric deposition (Bargagli et al., 2002). The problem with lichens is that they could reach a saturation point at which the elements can no longer be collected (Garty et al., 1993). In addition, the use of lichens could be influenced by climate or other environmental conditions (e.g., drought). Moreover, the sensitivity of lichens to sulfur dioxide (Nash, 2008) means that their use might be restricted in some places. Spiders, however, occur in all places (natural areas and industrialized ones) and so, their webs can be obtained easily. What is more, biomonitoring with spider webs provides good results even if the level of contamination is low. Therefore, it can be concluded that spider webs are more precise than lichens (Stojanowska et al., 2020). The advantage of lichens over the spider webs is in the durability, which means that the inappropriate location of spider web samples may lead to their quick destruction because they are fine and delicate. Moreover, lichens have been used in biomonitoring for many years, which makes them a well-known material, unlike spider webs, which are a new tool in biomonitoring studies. The lack of many studies of spider web accumulation might be an impediment, because it is hard to compare the obtained results with other studies.

The situation is similar to mosses, also commonly used in biomonitoring (Bargagli et al., 2002; Giordano et al., 2013;

Kosior et al., 2015; Liu et al., 2009). Mosses lack roots, epidermis, and cuticle layers. This allows them to absorb all nutrients, pollutants, and water from the air. They are widespread, can live in polluted environments for a long time, and have large surfaces (Blagnytė & Paliulis, 2010). The whole procedure of monitoring is simple and cost effective (Szczepaniak & Biziuk, 2003). All of these characteristics make them good indicators of air quality. One of the studies demonstrates that, compared with vascular plants, mosses could accumulate 3–51 times more PTEs in urban areas (Jiang et al., 2018). Mosses are useful in PTEs assessment but also in the determination of organic pollutants (e.g., Holoubek et al., 2000). Despite the many advantages of biomonitoring with mosses, there are some limitations, too. Mosses might be better than spider webs due to the durability of the material. However, the problem might occur with collecting mosses (the same problem as with lichens) from a clean area for transplantation. For instance, in northern countries, terrestrial mosses are covered by snow in winter (Lodenius, 2014). Thus, it could complicate the collection of mosses for transplantation, whereas with spider webs, the clean material can be obtained from laboratory-bred spiders. A further limitation is that, when mosses are used in the form of "moss bags" (i.e., mosses placed into mesh net bags or mats and hung in the air; Abulude & Elisha, 2017) to measure air pollution, the bags could dry out leading to changes in their efficiency in accumulating metals, depending on environmental conditions (Szczepaniak & Biziuk, 2003). Moreover, one study compares spider webs with mosses (van Laaten et al., 2020). Authors noticed higher mass fractions of selected elements in spider webs than in moss bags, although the webs were exposed for a shorter time. Therefore, it might be assumed that these two samplers are characterized by different mechanisms of particle retention. Considering that, the use of the spider webs can be recommended for short-term monitoring and mosses (or lichens) for observing long-term anthropogenic impacts.

Regarding the limitations of spider webs, we must mention the possibility of chemical incorporation from spiders' blood to spinnerets and finally to spider webs. This problem can be easily excluded by the use of spider webs obtained from spiders bred in clean laboratory conditions and the use of reference sites to establish the background concentrations and sampling artifacts.

PERSPECTIVES FOR FURTHER STUDIES

The increasing interest in the use of spider webs triggers many ideas for future studies. However, some issues are still unclear or unknown, and should be considered in future studies.

For instance, the use of spider webs in genotoxic studies is quite a new idea, but the researches described above (Rutkowski, Jadczyk, et al., 2018; Rutkowski et al., 2019) demonstrate that it is very promising. The low cost and ease of the sampling method is surely an encouraging factor. The common use of webs in genotoxicity studies would minimize the cost of such examinations.

Other prospering studies are those focused on the magnetic susceptibility of spider webs. Rachwał et al. (2018) concluded that magnetic biomonitoring using spider webs gives good results for airborne PM pollution. The analyses currently used for air pollution assessment are time consuming, although the promising idea of magnetic biomonitoring provides quick and reliable information about indoor and outdoor air quality. The biomagnetic studies are also inexpensive and nondestructive. Spider webs could be used in future as a complement to traditional air quality monitoring stations, which would be a valuable addition. Another idea is to use the spider webs for preliminary screening, which, unlike conventional measurements, is inexpensive and does not require qualified personnel.

Despite all these promising ideas for future studies, there are also some unexplained issues that have never been examined before. So, some questions remain unanswered. Are the spider webs as sufficient as other bioindicators, or are they better? Does rain wash away particles trapped on webs? Finally, are the pollutants inbuilt in the body of the spider and then transferred by spinnerets into the structure of the web itself? Comparison of webs with other bioindicators is a very interesting topic. One study focused on the comparison of the usefulness of spider webs with lichens in the accumulation of PTEs (Stojanowska et al., 2020). It was found that the accumulation in transplanted spider webs was far greater than in lichens and, in some cases, the differences were approximately one order of magnitude. Considering this, spider webs seem to be a better passive sampler than lichens, and so the web might be characterized as having greater sensitivity. According to these findings, it is proposed that spider webs could be used to recheck the quality of air in all places where the results from lichen analyses are below the detection limit. This issue, however, must be studied further to make sure the results obtained by Stojanowska et al. (2020) are repeatable. For mosses, we encountered a similar situation because only one study is available that recommends the use of the spider webs for short-term monitoring and mosses for long-term studies (van Laaten et al., 2020).

The studies comparing accumulation in a spider web with standard methods have been conducted twice (Rybak et al., 2015; Stojanowska et al., 2021). However, as presented in the studies mentioned above, such comparison is very difficult, and more studies are needed to fully understand the issue. This topic is essential in order to determine if the results from spider webs relate to the air quality standards for a given area. Obtaining such information would surely develop the topic and help to promote spider webs as commonly used tool in quantitative assessment.

The next uncertain issue concerns the process of washout particles from the surface of a spider web (external contamination). Similar studies, based on the use of human hair in bioindication, it is recommended to decontaminate the surface of the hair before analyses. For this purpose, organic solvents can be used but, in some studies, it is recommended to use just deionized water or water with shampoo

(Appenzeller & Tsatsakis, 2012). Observing this situation, it can be thought that the water from the rainfall could also remove some particles of pollution from the spider webs. It is not certain if we can treat human hair and a thread of spider as similar material and, therefore, if the water could remove the dust particles from the web. If so, the pollutants which remain on the web will derive only from the spider's body, not from the external deposition.

Additionally, the research mentioned above demonstrates that spider webs can be a very effective and useful tool in the identification of organic compounds, if we consider all the above-mentioned limitations (i.e., that they are not suitable for the indication of the most volatile PAH compounds and that the source of pollution may come from both external deposition and the accumulation of PAHs in the body of spiders from contaminated food). The PAH particles are deposited on the surface of the spider's web and penetrate its structure together with the dust. Surfactants or acid rain can remove only freshly deposited PAH particles, which, over time, diffuse into the protein and become bound. Toxicants derived from food are likely to have a secondary effect on spider web contamination.

For studies of PTEs and other elements on webs, as with hair, pollutants are washed out to a certain level, although some of them are permanently embedded in the matrix of the spider's web or come from inside the spider's body. Even if this is so, the results obtained using webs give much higher concentrations than lichens or mosses (Stojanowska et al., 2020; van Laaten et al., 2020). Therefore, we can conclude that the process of washing is not that destructive. However, this issue requires detailed research in the future. On the other hand, the nature of the web alone, which, although devoid of glue, forms a dense weave, favors the deposition of dust and other types of pollutants on its surface. The protein structure of the spider webs may also favor the accumulation of certain metals, as with bird feathers (Dmowski, 1999). Summing up, when interpreting the results of research on metals and elements on spider webs, it is necessary to emphasize their high versatility, but it is also necessary to consider many factors to avoid interpretation errors. Further, it is important to research where it would be possible to test the existence of a correlation between the content of metals in the web and the body of a studied spider. Little is known about the extent to which harmful substances present in the air are inbuilt in the body of the spider and then, with the use of spinnerets, into the structure of the web itself. This topic is crucial as it could affect the internal incorporation of pollution in the web structure. Peakall (1971) conducted an experiment in which the web building cycle of the Araneidae family was studied. These spiders are known to eat their old web. The research indicated that the newly constructed web contained approximately 80% of the material of the old, previously eaten web. The silk protein may be incompletely broken down in the digestive system (Peakall, 1971) and then incorporated into the new web.

However, most of the studies presented in this article are based on the use of spiders that do not eat old webs; thus, this kind of internal incorporation of toxins can be excluded. Despite that, some internal web pollution might occur as a result of the contamination of prey. Some of the spiders' victims are mobile and can come from distant areas, bringing contamination with them. This topic should be also considered in future studies because, at the moment, it is not well understood.

CONCLUSIONS

Numerous studies of spider webs prove that they can be a very useful tool in biomonitoring studies of air pollution and that they give good results in terms of PTE concentration as well as PAHs. What is more, spider webs can be used successfully in genotoxic studies (Ames test). The main advantage of the spider web as a bioindicator is that it can be easily obtained with almost no cost because it is widely abundant in both natural and urbanized areas. Moreover, the use of webs in monitoring does not produce any extra waste, and the amount of the web needed for analysis is very small. In contrast to other passive samplers, the spider web is a nonselective sampler and unlike most specific equipment, it does not need to be systematically controlled by qualified personnel. Despite the great potential of webs, it seems that it will still be a long time before this tool becomes widely used. The greatest disadvantage of the use of spider webs in biomonitoring is that there are still some issues, such as the washout of the particles from its surface or the incorporation of contamination into the web. Studies are few, which makes it difficult to compare the obtained results with others and to draw conclusions. There is also an issue connected with the comparison of spider webs with other bioindicators. A good understanding of this idea is crucial, and one day it may give us the answer whether the webs are better than other bioindicators. Furthermore, the current lack of studies correlating the contents of webs to professional measures of air quality, that is impactors and so forth, remains a critical gap indicating that this tool cannot be used as an independent, reliable tool for air monitoring and suggesting that studies of this type are very desirable and could bring a different perspective to using spider webs for air pollution studies in the future. On the other hand, perhaps it will not be possible to correlate both these approaches, and the application of spider webs will be limited to use in the same cases as other passive bioindicators, for example, mosses, lichens, and so forth with the difference that webs could be used independently of the season and applied much more effectively for selected air pollutants, for example PAHs.

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CONFLICT OF INTEREST

The authors declare no conflict of interest.

DATA AVAILABILITY STATEMENT

Data, associated metadata, and calculation tools are available from corresponding author Agnieszka Stojanowska (agnieszka.stojanowska@pwr.edu.pl).

SUPPORTING INFORMATION

Supporting infomrmation file contains the list of the articles focused on PTEs and PAHs analyses used in the process of creating this review article.

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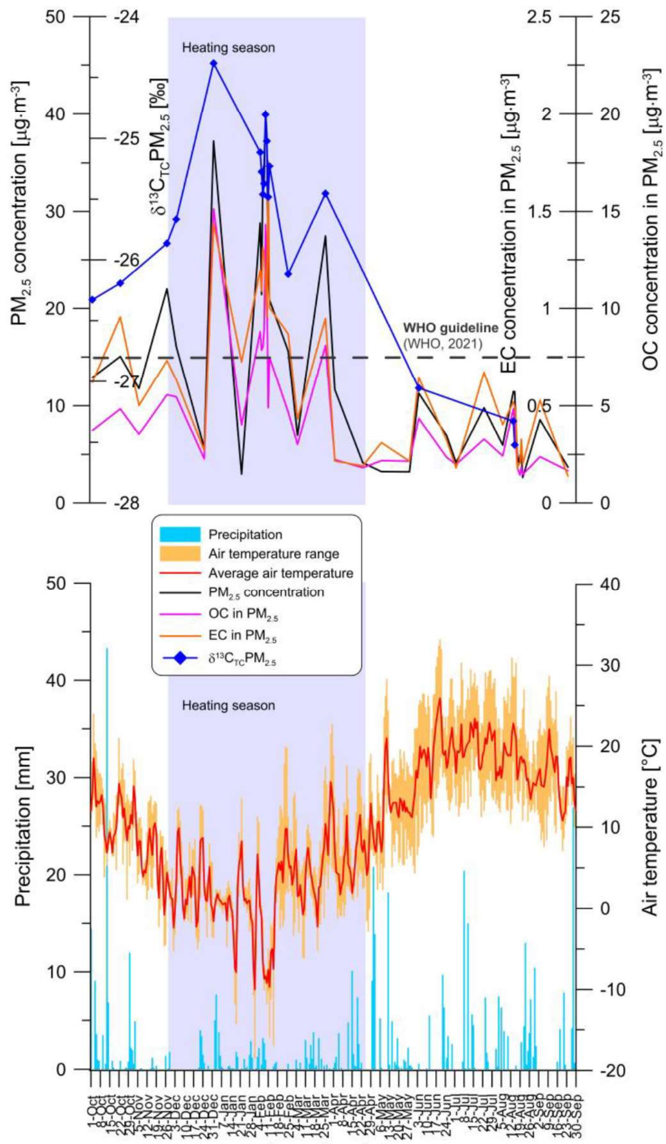
Artykuł 2

Innowacyjna praca wykorzystująca wiele niezależnych analiz w celu jak najdokładniejszego określenia jakości powietrza

The impact of seasonality and meteorological conditions on $PM_{2.5}$ carbonaceous fractions coupled with carbon isotope analysis: advantages, weaknesses and interpretation pitfalls. Maciej Górka, **Agnieszka Trzyna**, Anita Lewandowska, Anetta Drzeniecka-Osiadacz, Beata Miazga, Justyna Rybak, David Widory. *Atmospheric Research*. 2023, vol. 290, art. 106800, s. 1-17.

Głównym zadaniem wyżej wspomnianej pracy było przeprowadzenie złożonej analizy jakości powietrza w celu jak najlepszego scharakteryzowania źródeł pochodzenia cząstek węglonośnych w PMx. Badania obejmowały analizę frakcji $PM_{2,5}$, która pobrana została za pomocą pyłomierza (z głowicą $PM_{2,5}$) w okolicy huty miedzi w Legnicy w terminie od października 2020 do września 2021. Standardowo, w pierwszej kolejności w próbkach przeanalizowana została frakcja węglowa i relacje jej wzajemnych składników. Jednak samo zestawienie analizy składu izotopowego węgla ($\delta^{13}C$), zawartego w pyle, ze stężeniami frakcji węglowych (TC/OC/EC) może być czasami niewystarczające i prowadzić do mylnych wniosków. Stąd dołączenie dodatkowych analiz i wyników, takich jak: dane meteorologiczne, widma otrzymane za pomocą spektrometru furierowskiego w podczerwieni (FTIR), czy wyznaczenie pierwotnego węgla organicznego (OC_{prim}) oraz wtórnego węgla organicznego (OC_{sec}) w ogólnym OC, może być bardzo pomocne i odpowiedzieć na niejasności interpretacyjne. Stężenia $PM_{2,5}$, a także TC, OC oraz EC charakteryzowały się sezonową zmiennością z wyższymi wartościami otrzymanymi dla zimy (Rysunek 1), na co główny wpływ ma wzmożona niska emisja zanieczyszczeń oraz specyficzne niesprzyjające warunki meteorologiczne powodujące kumulację zanieczyszczeń atmosferycznych. Podobne obserwacje, wskazujące na sezonowość, zaobserwowano przy analizie składu izotopowego węgla ($\delta^{13}C$) w pyle. Zestawienie tych wniosków z widmami z analizy FTIR pozwoliło na wyciągnięcie wniosku, iż głównym źródłem zanieczyszczeń w okresie zimowym było niekompletne spalanie paliw kopalnych (w tym węgla kamiennego), natomiast latem dominowały cząsteczki biogeniczne oraz transport drogowy. Interesującym faktem jest wykazanie, iż stosunek OC/EC często stosowany jako dyskredytujący dane źródła zanieczyszczeń, może prowadzić do błędnych wniosków na temat sezonowości, jeżeli nie zostanie przetestowana jego statystyczna sezonowa zmienność. Finalnie, niniejsza praca dowodzi, iż tylko zastosowanie wielorakich analiz geochemicznych i ich wspólna interpretacja pozwoli na ominięcie potencjalnych błędów wnioskowania opartych na pojedynczym wskaźniku/interpretacji.

Wniosek: Złożona analiza zanieczyszczeń powietrza daje pewność, że wyciągnięte wnioski są poprawne. Badania potwierdziły sezonową zmienność zanieczyszczeń powietrza i wskazały, że zimą sytuacja warunkowana jest przez niską emisję oraz specyficzne warunki meteorologiczne, a latem przez *cząsteczki biogeniczne oraz transport drogowy.*



Rysunek 1 Roczne zmiany czasowe parametrów geochemicznych ($PM_{2,5}$, TC, OC, EC i $\delta^{13}C_{TC}$) i meteorologicznych (min/max/średnia temperatura i opady) w okresie od 01.10.2020 do 30.09.2021 (Górka et al., 2023).

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The impact of seasonality and meteorological conditions on $PM_{2.5}$ carbonaceous fractions coupled with carbon isotope analysis: Advantages, weaknesses and interpretation pitfalls

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A R T I C L E I N F O

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Carbonaceous fractions
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A B S T R A C T

$PM_{2.5}$ samples were collected from October 2020 to September 2021 in Legnica in the Lower Silesia Voivodeship (SW Poland), where environmental guidelines are often exceeded. In order to have a better insight into the respective inputs of local and regional sources concentrations of $PM_{2.5}$, carbonaceous fractions (TC/OC/EC), carbon isotope composition ($\delta^{13}C_{TC}$) and FTIR spectra of $PM_{2.5}$ were studied in parallel. The objectives of this study were to (i) identify the emission sources controlling the local aerosol budget and to (ii) discuss the potential limits of the approach used. We highlighted a seasonality in the concentrations of $PM_{2.5}$, TC, OC, and EC, with higher concentrations in winter resulting of an increased activity of local emission sources coupled to the occurrence of specific meteorological conditions. While we identified coal burning as the main source of pollution in winter, a mix of emissions from coal and bio/organic combustion and road traffic explains the pollution levels in summer. Coupling these findings with the study of FTIR spectra, we corroborated that incomplete combustion of fossil fuels is a major source in winter whereas biogenic particles are in summer. Despite the observed seasonal variations in the OC and EC concentrations, the OC/EC ratios did not show significant variations. It suggests that this ratio, if used as a single proxy to infer sources of carbonaceous aerosols, may lead to interpretation pitfalls. Our results strongly suggest that a multi-proxy approach that couples TC/OC/EC and FTIR to carbon isotope geochemistry provides a reliable evaluation tool for air quality and brings strong constraints on the corresponding sources of $PM_{2.5}$.

1. Introduction

Particulate matter (PM) is a mixture of solid and liquid particles suspended in the air (WHO, 2021). PM can vary in size and composition and these characteristics will depend on the implicated emission sources, weather conditions and potential secondary reactions in the studied area (Gelenceser et al., 2007). Among the major PM anthropogenic sources, the combustion of fossil fuels in industrial activities, emissions from residential buildings combusting fossil fuels for heating purposes and road traffic can be discriminated (Casotto et al., 2022; Juda-Rezler et al., 2020). Particles generated by these anthropogenic activities are mostly occurring in the fine fraction ($PM_{2.5}$; Bartz et al., 2021). They are not stopped in the nasal area when inhaled and can travel deep into the lungs, hence, posing a serious threat to human health (Hsu et al., 2016). The European Environment Agency (EEA, 2022) recently concluded that the $PM_{2.5}$ fraction is responsible for about 307,000 premature yearly deaths in the 27 EU Member States. The problem is particularly critical in Poland, which is responsible for an important share of the annual exceeding of the $PM_{2.5}$ European guidelines (EEA, 2020). In 2021 the average $PM_{2.5}$ concentration in Poland was 3.8 times higher than the recommended WHO annual air quality guideline (https://www.iqair.com/poland). This results in a high national mortality attributed to

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aerosol pollution: in 2018 and 2019 the number of deaths attributable to exposure to $PM_{2.5}$ in Poland accounted to 46.3 and 39.3 thousand people, respectively (Available online: https://www.statista.com/statistics/1284045/poland-exposure-to-pm25-deaths/ (accessed on 19.10.2022))(EEA, 2022). In Lower Silesia, a region that includes the city of Legnica, frequent exceeding of the annual WHO guideline of 15 μg $PM_{2.5}\cdot m^{-3}$ (WHO, 2021) has been reported within last decade (e.g. GIOŚ, 2011, 2015, 2018, 2022).

For $PM_{2.5}$ over Europe the typical carbonaceous fraction is 20–60% (e.g. Contini et al., 2018; Fuzzi et al., 2015; Vodička et al., 2022). The main components of this carbonaceous fraction are: (i) light-scattering organic carbon (OC) and (ii) light-absorbing elemental carbon (EC) (Galindo et al., 2019; Hussein et al., 2022), which sum up to form total carbon (TC). EC is a primary aerosol, which often occurs in soot and is directly created by the incomplete combustion of biomass or fossil fuels (Galindo et al., 2019). Defining the origin of OC is more difficult as it can derive from both anthropogenic and natural sources (Murillo et al., 2013). Moreover, OC can be divided into two sub-fractions: (i) primary organic carbon (OC_{prim}) emitted directly into the air by the combustion process and (ii) secondary organic carbon (OC_{sec}) created in the atmosphere by the secondary oxidation of volatile organic compounds (VOCs) by oxidants such as OH, NO_2, O_3 (e.g. Kucbel et al., 2016; Murillo et al., 2013).

Studies demonstrated the limitation of focusing on the sole measurement of the mass concentration of $PM_{2.5}$ carbonaceous fractions which may be insufficient for a precise determination of the main contributors (Viana et al., 2008), so in this study the attention was turned to the aerosol OC/EC ratio and additional measurements for a better understanding of the sources of contamination impacting regional air quality. Among the approaches complementing the study of the OC/EC ratio the study of the carbon stable isotope compositions ($\delta^{13}C$) of the aerosols has vastly demonstrated its added value for identifying the source(s) of TC in aerosols (e.g. Górka et al., 2020; Major et al., 2021; Masalaite et al., 2020; Vodička et al., 2022; Widory et al., 2004). Combining the OC/EC ratio with $\delta^{13}C$ is expected to provide a better identification of the specific sources of PM. $\delta^{13}C$ has demonstrated its potential for determining the share of anthropogenic sources, such as combustion (coal, liquid fuels in transports, biomass), and natural sources, such as organic fragments (plants, insects, etc.) (e.g. Bikkina et al., 2016; Górka et al., 2012, 2014, 2020; Kunwar et al., 2016). The $\delta^{13}C_{TC}$ for different C3 plants (i.e. plants in which the first carbon compound produced by photosynthesis contains 3 carbon: 3-phosphoglycerate) from SW Poland varied between −30.5 and − 27.3‰ (Górka et al., 2009; Górka and Jędrysek, 2008). $\delta^{13}C_{TC}$ for liquid fuels vary geographically and depend on the origin of the refined petrol (Masalaite et al., 2012). For example, in Paris (France) Widory et al. (2004) reported an average $\delta^{13}C$ of −24.2 ± 0.6‰ for particles from the combustion of unleaded gasoline and of −26.5 ± 0.5‰ for those by diesel, whereas in Wroclaw (Poland) these gasolines generated particles with $\delta^{13}C$ of −26.8‰ and − 28.3‰, respectively (Górka and Jędrysek, 2008). Górka and Jędrysek (2008) reported a $\delta^{13}C_{TC}$ of −24.5‰ for particles from the incomplete combustion of polish coal. This has to be in perspective to the average $\delta^{13}C$ of −23.9 ± 0.3‰ for polish coal (Upper Silesia coal basin; (Kotarba and Clayton, 2003)) and of −25.9 ± 0.2‰ for lignite deposits in Poland (Kosztowniak et al., 2016). Widory (2006) demonstrated that the carbon isotope fractionation ($\delta^{13}C$) between solid fuel (coal) and particles during incomplete combustion is −0.3 ± 0.9‰, which would partly account for this isotope difference in coal combustion. Górka and Jędrysek (2008) observed a similar isotope difference between coal and coal soot. Hence, it can be expected that the $\delta^{13}C_{TC}$ of particles from the combustion of lignite should be similar to that of the initial lignite. Similarly, the coke combusted in smelters, deriving from the production of coal, should display similar $\delta^{13}C_{TC}$ to the initial coal. However, due to the geographical variations in the $\delta^{13}C_{TC}$ for specific sources, the use of particle $\delta^{13}C$ to identify contamination sources should rather be based, when possible, on the characterization of local emissions rather than more global ones to avoid potential misinterpretations. One should also consider the difficulty arising from overlapping ranges for $\delta^{13}C$ between different emission sources that may render untangling the $\delta^{13}C$ signal challenging (e.g. Stojanowska et al., 2021).

Fourier-Transform InfraRed (FTIR) spectroscopy has also proven that it can successfully monitor air pollutants (e.g. Shankar et al., 2022; Usman et al., 2022). For example, this has been used to detect inorganic compounds (e. g. ammonium nitrate or calcium sulphate) in aerosols (Varrica et al., 2019). FTIR spectrum relies on absorption peaks, corresponding to the vibration frequencies among the different atom bonds in nanoparticles. Due to their specific physical structures a variety of pollutants can thus be distinguished (Wei et al., 2020).

In the present study we conducted the analysis of $PM_{2.5}$ samples collected from October 2020 to September 2021 in the area of the city of Legnica city (SW Poland). We selected this region as it frequently faces exceeding concentrations of $PM_{2.5}$ and of arsenic in PM_{10} (GIOŚ, 2021, 2022). The annual mean $PM_{2.5}$ concentration in Legnica in 2020 was 16.2 $\mu g\cdot m^{-3}$ (GIOŚ, 2021) and 18 $\mu g\cdot m^{-3}$ in 2021 (GIOŚ, 2022). Both these values are superior to the latest annual WHO guidelines of 5 $\mu g\cdot m^{-3}$ (WHO, 2021). In this case, a specific location of Legnica influences the deterioration of the air quality. This may be attributed to the proximity of the GIOŚ monitoring station with a copper smelter (KGHM - Copper Mining and Metallurgical Combine), the express national road (S3) and highway (A4), and the nearby households that daily combust fossil fuels. As previously discussed, coupling the concentrations of aerosol carbonaceous fractions (TC/OC/EC) with the TC carbon isotope compositions can already bring constraints on the emission sources (e.g. Górka et al., 2020; Stojanowska et al., 2021) but here we aimed at providing even more precise constraints by pairing additional parameters: OC_{prim} (primary organic carbon) and OC_{sec} (secondary organic carbon), meteorological data and FTIR spectra.

2. Materials and methods

2.1. Study area

The study was carried out in Legnica, a city of 98.000 inhabitants (Available online: https://stat.gov.pl/ (accessed on 19.10.2022)), located in the Legnica–Głogów Copper District in south-western Poland (Lower Silesia voivodship). Potential sources of air contamination in Legnica are connected with local sources (i.e. industrial activities, home heating and road traffic) as well as with long-range transport from outside the city. Copper mining and a metal processing plant (KGHM - Copper Mining and Metallurgical Combine) is located west of the city center (Fig. 1). This company is considered the first silver producer and the sixth producer of electrolytic copper in the world. The heating system in Legnica consists of: (i) two heating plants supplying the municipal heating network, the Central Heating Plant located in the northeastern part of the city runs 4 fine coal-fired boilers with a total capacity of 165.26 MWT and the "Górka" Heating Plant located in the eastern part of the city runs 2 fine coal-fired boilers with a total capacity of 23.26 MWT); (ii) 4 gas-fired local boiler houses with respective capacities of 24kWT, 180 kWT, 340 kWT, 70kWT; (iii) multiple individual heating sources (Official Journal of the Lower Silesian Voivodeship, item 4539). Due to the close proximity of these heating plants we hypothesized that they may have a major impact on air quality in this selected region. Many heavy traffic roads surround Legnica (Fig. 1): the national road #94 (∼7000 vehicles/day), the express national road S3 westward (∼18,000 vehicles/day), and the highway A4 southward (∼30,000 vehicles/day)(https://stat.gov.pl/en/). The contribution of road traffic to the $PM_{2.5}$ local budget is estimated at 13% (Mikołajczyk et al., 2017).

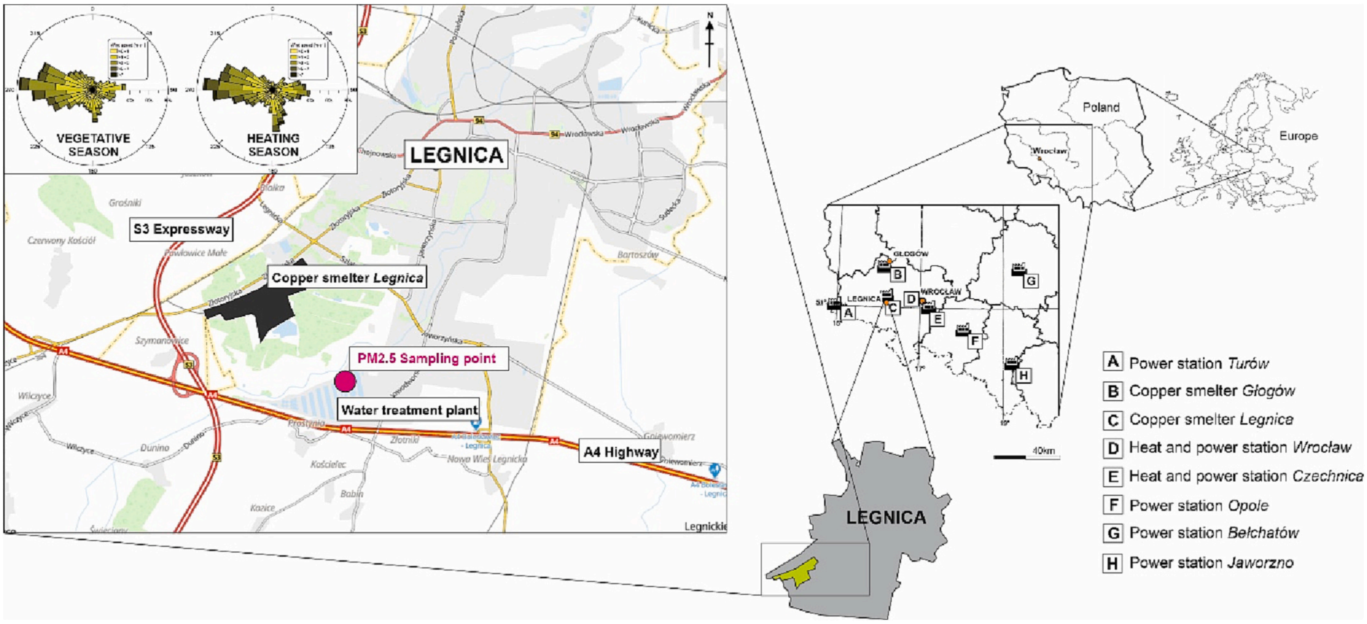

Fig. 1. Location of the sampling points in the vicinity of Legnica city. Wind roses for the vegetative and heating seasons are also reported for the 01.10.2020–30.09.2021 period.

2.2. Sampling methodology

Daily $PM_{2.5}$ samples were collected twice per month between 02.10.2020 and 24.09.2021 (Table 1). Additionally, two one-week daily aerosol sampling campaigns were conducted in winter (06–12.02.2021) and summer (14–20.08.2021). Samples were collected on 150 mm diameter QMA quartz filters (Whatman® QMA) using a DHA-80 high-volume sampler (Digitel®) placed in the area of the city water treatment plant (51.169 N, 16.133 E; Fig. 1). QMA quartz filters were conditioned in a desiccator before and after sampling following the PN-EN 12341 norm. Weighted quartz filters were transported directly to the $PM_{2.5}$ sampler. For this study, a total of 38 $PM_{2.5}$ samples were collected. Samples were discriminated according to their season of collection: (i) heating season (between 27.11.2020 and 02.04.2021) and (ii) vegetative season (between 02.10.2020 and 06.11.2021 and between 23.04 and 24.10.2021). The vegetative season is defined as the period when the daily average temperature exceeds 5 °C (Tomczyk and Szyga-Pluta, 2019). Days not corresponding to the vegetative season were considered as the heating season.

2.3. Meteorological parameters

Meteorological parameters (temperature, pressure, precipitation, relative humidity and wind speed) for the period 01.10.2020–30.09.2021 were gathered at the Institute of Meteorology and Water Management—National Research Institute (IMGW-PIB) synoptic station located in Legnica (51.193 N, 16.207 E). The precision of the meteorological measurements conformed with the guidelines of the World Meteorological Organization (WMO, 2021). Meteorological measurements were uploaded using an *R* package (R Core Team, 2013) to access the free in-situ meteorological datasets (Czarnecki et al., 2020). The $PM_{2.5}$ concentrations in the air were simultaneously monitored at a nearby urban station (Available online: https://powietrze.gios.gov.pl (accessed on 19.10.2022)) operated by the Chief Inspectorate of Environmental Protection (CIEP). Synoptic charts were prepared using the Royal Netherlands Meteorological Institute model (KNMI; https://www.knmi.nl; KNMI is not involved in the derivative work and does not necessarily endorse its purport).

In addition to the above parameters, wind roses were created to determine the direction of potential sources of pollution using Grapher 10.0 Golden Software (Fig. 1), and the movement of air masses using the HYSPLIT model developed by NOAA (Rolph et al., 2017; Stein et al., 2015) (Available online: www.arl.noaa.gov/ready/hysplit4.html (accessed on 19.10.2022)). For each sampling period 48-h airmass backward trajectories were calculated at 6 h intervals, at a 50 m height above the ground level. The calculated trajectories are detailed in (Lewandowska et al., 2010; Lewandowska and Falkowska, 2013). We generated wind roses by processing data collected by the Institute of Meteorology and Water Management - National Research Institute.

2.4. Analytical procedures

2.4.1. Determination of the $PM_{2.5}$ concentrations

The $PM_{2.5}$ mass concentrations were determined at the laboratory of the Voivodship Inspectorate for Environmental Protection (VIfEP) in Legnica according to the Polish guidelines for assessing the levels of substances in the air and the European Union Directive CAFE (European Parliament; European Parliament, 2008). The PN-EN 1234 reference weighting method was used. Prior to sampling, filters were first conditioned in desiccators for three days and weighted at a temperature between 19 and 21 °C and a relative humidity between 45 and 50%. The same procedure was followed after sampling. Finally, $PM_{2.5}$ concentrations were expressed in μg per m^3 of filtered air.

2.4.2. Determination of the total, organic and elemental carbon concentrations

Organic carbon (OC), elemental carbon (EC) and total carbon (TC) concentrations in all $PM_{2.5}$ samples were measured by thermo-optical method on a Sunset Laboratory Dual-Optical Carbonaceous Analyzer. A 1.5 cm^2 piece was cut from the sample quartz filter. $PM_{2.5}$ were thermally desorbed from the filter medium, under an inert helium atmosphere, and oxidized using carefully controlled heating ramps. Concentrations were determined on a flame ionization detector (FID). The analysis was conducted in accordance with the EUSAAR2 protocol (including pyrolysis process), owing to the optimal maximum temperature obtained at the end of the first stage (OC analysis), which amounted to 650 °C and ensured that only 2.5 ± 2.4% of elemental carbon was combusted during that stage of analysis (Cavalli et al.,

Table 1
Geochemical and meteorological data for samples collected in Legnica (SW Poland) during a 1-year campaign between the 2nd of October 2020 and the 24th of September 2021.

Sampling date	$PM_{2.5}$ [$\mu g \cdot m^{-3}$] CIEP Legnica	$PM_{2.5}$ [$\mu g \cdot m^{-3}$]	TC [$\mu g \cdot m^{-3}$]	OC [$\mu g \cdot m^{-3}$]	EC [$\mu g \cdot m^{-3}$]	OC/EC	OC_{prim} [$\mu g \cdot m^{-3}$]	OC_{sec} [$\mu g \cdot m^{-3}$]	$\delta^{13}C$ [‰]	1/TC	T [°C]	Precipit. [mm]	Wind speed [$m \cdot s^{-1}$]	RH [%]	Press. [hPa]
02.10.2020[v]	14.6	12.9	4.4	3.7	0.6	6.0	2.80	0.94	−26.33	0.230	14.2	0.0	3.0	91.0	988.0
23.10.2020[v]	21.8	15.1	5.8	4.8	1.0	5.1	4.31	0.52	−26.19	0.173	14.2	0.9	2.0	82.8	998.3
06.11.2020[v]	17.6	11.8	4.0	3.5	0.5	7.1	2.26	1.27	n.d.	0.248	8.3	0.0	3.9	83.5	1018.7
27.11.2020[h]	32.1	22.0	6.3	5.6	0.7	7.6	2.04	3.53	−25.86	0.159	4.4	0.0	1.6	93.3	1006.9
04.12.2020[h]	12.4	16.1	6.1	5.5	0.6	8.6	1.76	3.69	−25.67	0.164	3.5	0.0	2.6	79.4	984.2
25.12.2020[h]	5.8	5.7	2.5	2.3	0.3	8.4	0.75	1.52	n.d.	0.393	2.7	0.7	3.5	88.6	1000.1
01.01.2021[h]	42.8	37.2	16.6	15.1	1.4	10.5	3.99	11.13	−24.38	0.060	−1.6	0.0	1.8	94.1	993.8
22.01.2021[h]	15.0	3.0	4.8	4.0	0.7	5.6	2.02	2.02	n.d.	0.210	8.3	0.1	4.3	66.1	981.7
05.02.2021[h]	32.3	28.8	10.0	8.8	1.2	7.4	3.32	5.47	−25.11	0.100	0.1	0.0	4.0	90.5	1003.9
06.02.2021[h]	19.6	21.4	8.9	7.9	1.1	7.2	3.03	4.83	−25.28	0.112	−1.1	0.5	4.5	73.0	1003.1
07.02.2021[h]	20.0	34.0	9.3	8.0	1.3	6.1	3.65	4.37	−25.46	0.107	−6.7	3.2	5.5	79.9	996.4
08.02.2021[h]	26.3	34.9	10.2	8.9	1.3	7.0	3.54	5.35	−25.37	0.098	−8.7	2.7	0.0	81.5	986.8
09.02.2021[h]	52.5	40.3	15.4	14.3	1.1	12.7	3.13	11.17	−24.81	0.065	−8.4	1.0	0.0	83.9	989.8
10.02.2021[h]	50.7	37.7	12.5	11.6	1.0	12.1	2.65	8.91	−25.02	0.080	−9.2	0.0	2.4	81.4	995.0
11.02.2021[h]	33.4	23.7	6.7	4.9	1.8	2.8	4.90	0.00	−25.48	0.150	−7.6	0.0	3.1	76.9	1008.1
12.02.2021[h]	34.7	20.9	8.5	7.5	1.0	7.5	2.79	4.69	−25.23	0.118	−9.7	0.0	3.5	83.1	1017.4
26.02.2021[h]	27.3	15.6	5.5	4.7	0.9	5.4	2.41	2.27	−26.12	0.180	6.3	0.6	2.6	82.1	1012.5
05.03.2021[h]	12.7	7.0	3.4	3.0	0.4	7.0	1.20	1.82	n.d.	0.290	1.5	0.1	3.1	74.0	1007.3
26.03.2021[h]	44.3	27.4	9.0	8.1	0.9	8.5	2.64	5.45	−25.45	0.111	10.4	0.0	1.6	69.4	1004.7
02.04.2021[h]	13.0	11.6	2.4	2.2	0.2	10.3	0.60	1.63	n.d.	0.408	7.2	0.7	4.0	77.3	1002.5
23.04.2021[v]	10.0	4.1	2.0	1.8	0.2	9.5	0.86	0.96	n.d.	0.497	7.0	0.0	4.9	67.9	1008.4
07.05.2021[v]	7.6	3.2	2.5	2.2	0.3	7.0	1.40	0.78	n.d.	0.401	7.0	0.2	3.8	81.9	994.1
28.05.2021[v]	5.3	3.2	2.4	2.1	0.2	10.0	0.97	1.18	n.d.	0.423	11.8	0.4	3.8	81.9	1004.6
04.06.2021[v]	13.0	11.3	5.0	4.4	0.6	6.7	2.91	1.44	−27.05	0.200	17.7	0.6	2.3	68.6	1007.8
25.06.2021[v]	8.4	6.9	2.7	2.3	0.3	7.3	1.45	0.89	n.d.	0.375	17.3	1.2	1.4	85.0	1002.7
02.07.2021[v]	6.6	4.2	2.2	2.0	0.2	11.0	0.82	1.17	n.d.	0.461	16.7	0.0	3.0	82.9	1000.0
23.07.2021[v]	16.7	9.8	4.0	3.3	0.7	4.9	3.04	0.25	n.d.	0.253	19.4	0.0	0.9	67.5	1002.6
06.08.2021[v]	7.7	6.0	2.8	2.4	0.4	6.0	1.82	0.60	n.d.	0.354	17.4	0.0	2.6	76.3	991.9
14.08.2021[v]	17.1	11.4	5.4	4.8	0.5	9.3	2.35	2.50	−27.33	0.186	22.8	0.0	2.6	63.3	1004.4
15.08.2021[v]	14.8	11.4	4.6	4.1	0.5	8.3	2.25	1.90	−27.52	0.215	21.9	0.0	2.3	64.9	999.5
16.08.2021[v]	12.0	8.2	3.4	3.0	0.4	6.9	1.94	1.01	n.d.	0.295	21.0	0.4	3.9	68.4	993.5
17.08.2021[v]	6.6	4.9	2.0	1.8	0.2	10.1	0.81	1.00	n.d.	0.505	15.9	0.0	5.4	63.1	998.4
18.08.2021[v]	6.3	3.9	1.8	1.6	0.2	8.0	0.92	0.70	n.d.	0.547	16.9	0.0	5.1	62.6	999.1
19.08.2021[v]	8.0	5.0	1.7	1.4	0.2	7.0	0.93	0.52	n.d.	0.606	18.5	0.0	3.6	69.3	998.8
20.08.2021[v]	8.1	4.9	2.2	1.9	0.3	5.6	1.48	0.37	n.d.	0.459	18.7	2.8	2.4	76.4	1001.5
27.08.2021[v]	4.7	2.6	1.7	1.5	0.2	7.3	0.91	0.56	n.d.	0.600	18.0	0.0	1.6	74.3	1004.7
03.09.2021[v]	13.7	8.6	2.9	2.4	0.5	4.5	2.38	0.00	n.d.	0.343	17.2	0.0	2.6	77.4	1005.5
24.09.2021[v]	6.3	3.7	1.8	1.7	0.1	12.0	0.63	1.04	n.d.	0.553	15.1	0.0	6.6	68.1	997.9
Minimum	4.7	2.6	1.7	1.4	0.1	2.8	0.60	0.00	−27.5	0.060	−9.7	0.0	0.0	62.6	981.7
Maximum	52.5	40.3	16.6	15.1	1.8	12.7	4.90	11.17	−24.4	0.606	22.8	3.2	6.6	94.1	1018.7
Mean	18.5	14.2	5.4	4.7	0.6	7.7	2.15	2.56	−25.8	0.282	8.6	0.4	3.0	77.1	1000.4
Median	14.2	11.4	4.2	3.6	0.5	7.3	2.14	1.36	−25.5	0.239	9.4	0.0	3.0	77.4	1000.8
SD	13.0	11.2	3.8	3.4	0.4	2.2	1.10	2.81	0.8	0.163	9.9	0.8	1.4	8.7	8.1

n.d. no data.
v vegetative season.
h heating season.

2010). Automatic calibration with an internal standard (5.0% methane in equilibrium with analytically pure He) took place always at the end of the second stage of the analysis (EC analysis). Additionally, after every 10–15 samples, an external standard was analyzed (99% analytically pure sugar solution). The general QA/QC performance carbon standard solution concentration was 4.207 μg C/μl. A low-level working standard solution at 1.050 μgC/μl was also used for calibration purposes. Both standard solutions were stored in a glass vial with Teflon cap line in the refrigerator for <6 months. The detection limit of the method was 0.3 μg per cm^2 for both OC and EC ($n = 72$) and the corresponding analytical error was <6% for EC and < 10% for OC (with a 99% confidence interval). The blank sample value for OC was <3.0 $μg·cm^{-2}$ of the filter, while for elemental carbon it was below the detection limit of the method. All OC and EC concentrations for $PM_{2.5}$ samples were corrected for blank values (Lewandowska et al., 2018; Wiśniewska et al., 2017; Witkowska et al., 2016; Witkowska and Lewandowska, 2016).

Pio et al., 2011 and Juda-Rezler et al. (2020) proposed the minimum slope method to estimate the distribution of the OC mass between primary (OC_{prim}) and secondary (OC_{sec}) organic carbon using the following equations (Eqs. (1) and (2)), based on the characterization of the minimal OC/EC ratio:

$$OC_{sec} = OC_{total} - \left(\frac{OC}{EC}\right)_{min} \times EC \quad (1)$$

$$OC_{prim} = OC_{total} - OC_{sec} \quad (2)$$

Here, as the minimal OC/EC ratio presented large variations between the heating ($OC/EC_{min} = 2.78$) and vegetative ($OC/EC_{min} = 4.52$) seasons, we elected to calculate OC_{prim} and OC_{sec} values for each of the seasons (Table 1).

2.4.3. Determination of the carbon stable isotope compositions ($\delta^{13}C$)

$\delta^{13}C$ were measured at the University of Wrocław using a combustion module (CM) coupled with a cavity ring-down spectroscopy (CRDS) system (G2201-i analyzer, Picarro Inc.®). A thin layer containing the $PM_{2.5}$ was manually cut from the top of the filter and placed into a tin 9 × 5 mm standard weight capsule that was sealed. After the sample was flash combusted at 980 °C, the generated purified CO_2 was collected using an interface (N_2 carrier gas) and sent to the isotope analyzer via the Liason® interface. Liu et al. (2018) showed that C concentrations and the final $\delta^{13}C$ obtained by this technique are dependent. As our $PM_{2.5}$ samples showed variable C contents, we corrected for this bias by analyzing a sample of known amount in each run that was adjusted to obtain signal similar to that of the CO_2 standard peaks. All $\delta^{13}C$ values were reported after correction by a multi-point normalization (Coplen et al., 2006; Skrzypek, 2013) to the VPDB scale, based on international standards NBS-19, NBS-18, IAEA CO-8, USGS-24, USGS-40, and USGS-44. For a greater spread and more precisely normalized $\delta^{13}C$ values, an internal laboratory standard was prepared based on a 6-point international standard calibration curve (Ciesielczuk et al., 2021). Therefore, a maximum 11-point calibration curve was used to increase as much as possible the precision of the CM-CRDS measurements and final normalization. Analytical uncertainty on $\delta^{13}C$ was <0.1‰.

2.4.4. Isotope Mass Balance calculation

Isotope Mass Balance (IMB) calculation has been performed in order to estimate the respective contributions of the different endmembers controlling the carbon budget in the aerosol samples. Details about the IMB calculation are provided in Górka et al. (2020) and Górka et al. (2014).

2.4.5. FTIR analysis

A total of four samples were used for the FTIR analysis. About 1.5 mg of $PM_{2.5}$ aerosols were scraped from the filter and homogenized in an agate mortar sample, and mixed with 200 mg spectral pure KBr. The pellet techniques was then used (Ingebrigtson and Smith, 1954). A piece of a clean filter was prepared the same way and used as a reference sample. The analysis was conducted using a Thermo Scientific Nicolet 380 FT-IR (Fourier Transform Infra-Red) Spectrometer. The spectrometer is equipped with a deuterated triglyceride sulphate detector and the OMNIC software. Spectra were recorded at 4 cm^{-1} resolution and 4000–400 cm^{-1} spectral range. For each sample 256 scans in transmission mode were obtained.

2.4.6. Statistical analysis

The normality of the dataset was evaluated using the Shapiro-Wilk's W test. Spearman's correlation coefficients (Sokal and Rohlf, 2012) were calculated to examine the relationship between the geochemical and meteorological data. Differences among the sampling periods (heating and vegetative) for the measured geochemical parameters were assessed by one-way analysis of variance ANOVA and Kruskal–Wallis test by ranks. For normal distributions, the homogeneity of variances was checked with a Levene test. Post-hoc the HSD Tukey test was applied to check the statistical signification of differences between carbonaceous species concentration in the two independent groups of samples. For groups not showing a normal distribution, the Kruskal–Wallis one-way analysis of variance and multiple comparisons of mean ranks were applied (Sokal and Rohlf, 2012). The above calculations as well as descriptive statistics were done using TIBCO Statistica® 13.3.0 software (TIBCO Statistica, 2017; Available online: https://www.tibco.com/products/tibco-statistica (Accessed on 09.09.2022)).

3. Results

3.1. $PM_{2.5}$ mass concentrations

Fig. 2 and Table 1 report the temporal variability of $PM_{2.5}$ mass concentrations in Legnica between 01.10.2020 and 30.09.2021. $PM_{2.5}$ concentrations varied from 2.6 to 40.3 $μg·m^{-3}$ (average 14.2 ± 11.2 $μg·m^{-3}$). During the sampling period the daily $PM_{2.5}$ guideline of 15 $μg·m^{-3}$ (WHO, 2021) was exceeded 14 times, which represents 37% of the measuring period (Table 1 and Fig. 2): 13 times during the heating season and only once during the vegetative season. These aerosol concentrations are in good agreement with those obtained for the same period at Legnica CIEP station (Pearson correlation coefficient $r = 0.89$; $p < 0.001$). Air monitoring data at the CIEP identified 17 days exceeding the $PM_{2.5}$ WHO guideline, which represents 45% of the measuring days, among which 13 were recorded during the heating season (Table 1).

The average $PM_{2.5}$ concentration was 22.8 ± 11.5 $μg·m^{-3}$ in the heating season and 7.3 ± 11.5 $μg·m^{-3}$ during the vegetative one. When compared to other data observed in the country, these $PM_{2.5}$ concentrations are slightly lower than those reported for Warsaw 27.0 and 11.5 $μg·m^{-3}$ (Juda-Rezler et al., 2020), significantly lower than those in Kraków 47 ± 24 and 18 ± 5 $μg·m^{-3}$ (Samek et al., 2020). However they are much higher than those reported for Gdańsk 3.7 ± 1.6 and 3.5 ± 1.8 $μg·m^{-3}$ (Witkowska and Lewandowska, 2016).

3.2. Carbon fractions (TC/OC/EC) in $PM_{2.5}$

TC concentrations are reported in Table 1, and EC and OC concentrations are shown in Fig. 2 and Table 1. TC varied from 1.7 to 16.6 $μg·m^{-3}$ (average 5.4 ± 3.8 $μg·m^{-3}$), OC from 1.4 to 15.1 $μg·m^{-3}$ (average 4.7 ± 3.4 $μg·m^{-3}$), and EC from 0.1 to 1.8 $μg·m^{-3}$ (average 0.6 ± 0.4 $μg·m^{-3}$). Values obtained in Legnica are similar (slightly lower) to those obtained in Warsaw (Juda-Rezler et al., 2020) where the annual average OC is 5.56 $μg·m^{-3}$ and EC 1.47 $μg·m^{-3}$. Interestingly, concentrations reported for non-urban sites (Złoty Potok and Racibórz, both located in southern Poland) by Błaszczak et al. (2016) were significantly higher than our results for an urban site. The authors reported OC concentrations of 8.58 and 12.08 $μg·m^{-3}$ and EC ones of 1.48 and 1.96 $μg·m^{-3}$, respectively, for Złoty Potok and Racibórz.

In Legnica, the seasonal averages for the vegetative and heating

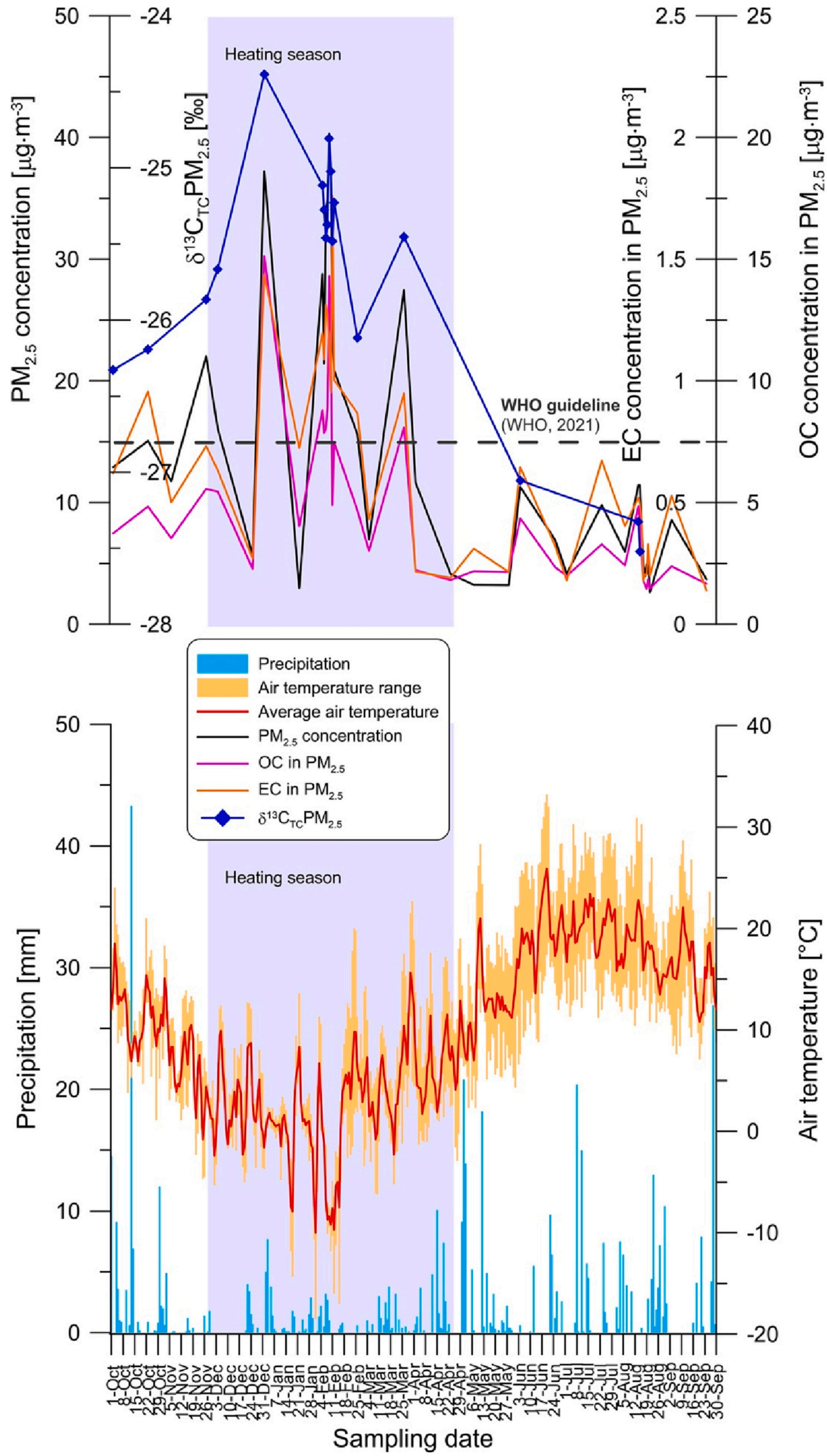

Fig. 2. Yearly temporal variations of geochemical ($PM_{2.5}$, TC, OC, EC and $\delta^{13}C_{TC}$) and meteorological (min/max/average temperature and precipitation) parameters between 01.10.2020 and 30.09.2021.

seasons were 2.7 ± 1.1 $\mu g \cdot m^{-3}$ and 7.2 ± 3.7 $\mu g \cdot m^{-3}$ for OC, whereas they were 0.4 ± 0.2 $\mu g \cdot m^{-3}$ and 0.9 ± 0.4 $\mu g \cdot m^{-3}$ for EC, respectively. The calculated OC_{sec} for the vegetative season was 0.93 ± 0.54 $\mu g \cdot m^{-3}$ and the corresponding OC_{prim} 1.77 ± 0.94 $\mu g \cdot m^{-3}$. It comes that 65.5% of the OC mass was deriving from primary sources and 34.5% from secondary ones. For the heating season the calculated OC_{sec} was 4.58 ± 3.14 $\mu g \cdot m^{-3}$ and the OC_{prim} 2.61 ± 1.11 $\mu g \cdot m^{-3}$. This shows an opposite trend to the vegetative season with 36.3% of the OC mass deriving from primary sources and 63.7% from secondary ones. The winter period is thus characterized by OC_{prim} and OC_{sec} values 1.5 and 4.9 times higher, respectively, compared to summer. Juda-Rezler et al. (2020) observed a similar increase from summer to winter in Warsaw for OC_{prim} (1.7 times) but lower for OC_{sec} (2.8 times). Still, this increase of OC_{sec} inputs during winter is in agreement with the findings of previous studies (Cesari et al., 2018; Kim et al., 2019; Tiwari et al., 2014).

3.3. Total carbon isotope composition ($\delta^{13}C_{TC}$) of $PM_{2.5}$

Seasonal variations of the total carbon isotope compositions ($\delta^{13}C_{TC}$) observed at the Legnica station are presented in Fig. 2 and in Table 1. During the study period $\delta^{13}C_{TC}$ varied from −27.5 (15.08.2021) to −24.4‰ (01.01.2021), with an average of −25.8 ± 0.8‰. For winter, the average $\delta^{13}C_{TC}$ was −25.3 ± 0.4‰, while for the summer it decreased to −26.9 ± 0.5‰. These values are in agreement with those recently observed elsewhere in Europe, e.g. Vilnius, Lithuania (Masalaite et al., 2017, 2020), Debrecen, Hungary (Major et al., 2021) or Prague, Czech (Vodička et al., 2022). The $\delta^{13}C_{TC}$ measured for the PM_{10} aerosol fraction collected at the same CIEP station in 2011 (Górka et al., 2020) also showed a very similar seasonality with isotope compositions ranging from −27.7‰ (15.07.2011) to −25.2‰ (21.01.2011) and an average of −26.7 ± 0.9‰.

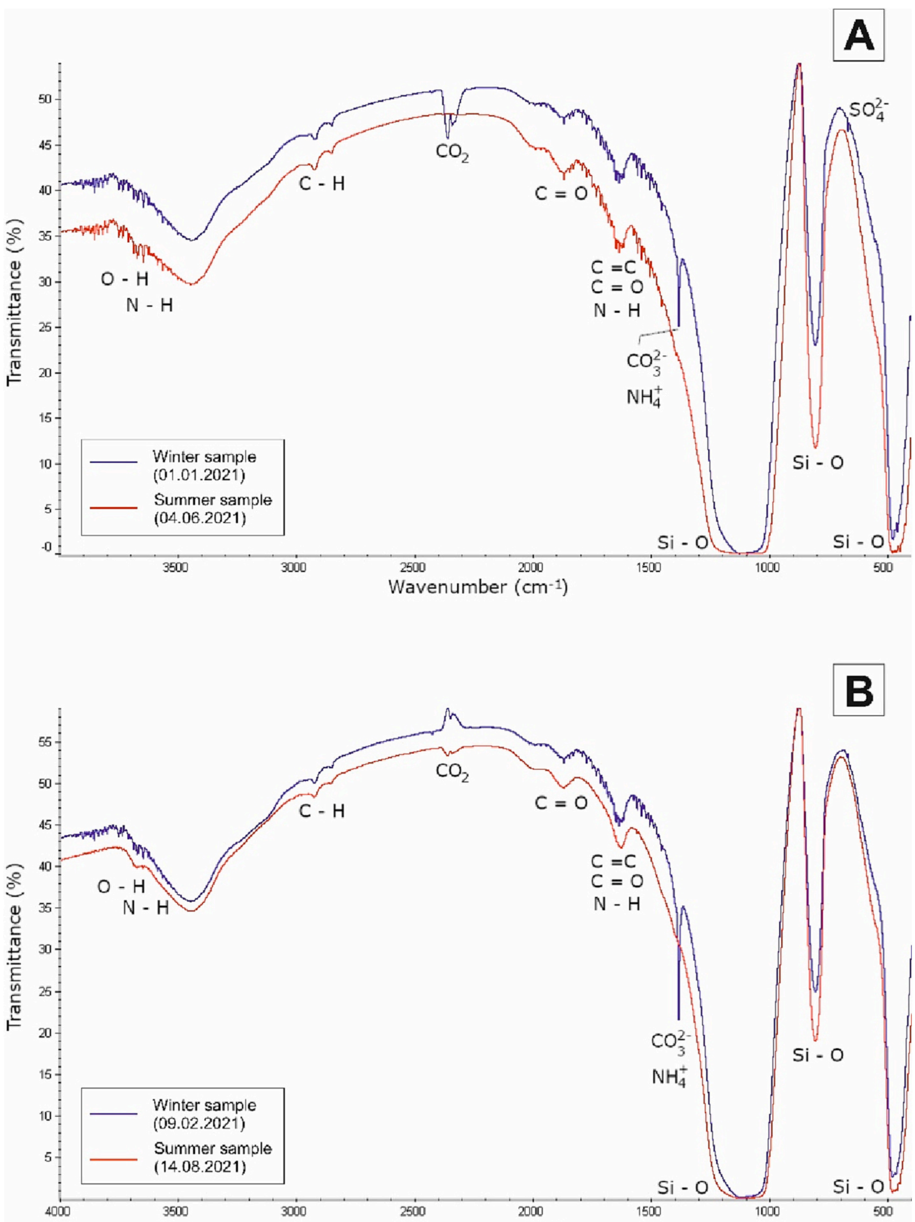

Fig. 3. FTIR spectra of [A] $PM_{2.5}$ filters collected during selected sampling days in winter and summer; [B] $PM_{2.5}$ filters collected during one-week episode in winter and summer.

3.4. FTIR spectra

Fig. 3 reports the FTIR spectra obtained for $PM_{2.5}$ samples collected during one-week sampling periods in winter and summer. Results indicate the presence of both organic and inorganic substances. For the sample collected during the heating season (01.01.2021 – Fig. 3A) several weak peaks appear in the region >3000 cm^{-1}, where typically signals of the O—H, hydrocarbons (C—H vibrations) or amine (N—H) groups are observed. Aliphatic hydrocarbons (*n*-alkanes; C—H stretching) are typically present between 2925 and 2855 cm^{-1}. Moreover several, but not strong, stretching double bonds are recorded in the region at 1900–1700 cm^{-1}, where the signals of C═O bound in carboxylic acids, anhydrite and ketones or aldehydes, are visible. The next is at ~1630 cm^{-1}, which belongs to the aromatic C═C bonds in various compounds, e.g. aromatic amines (Shankar et al., 2022). The 1630 cm^{-1} is connected to an aromatic ring as suggested by Szczepaniak (2002). Ji

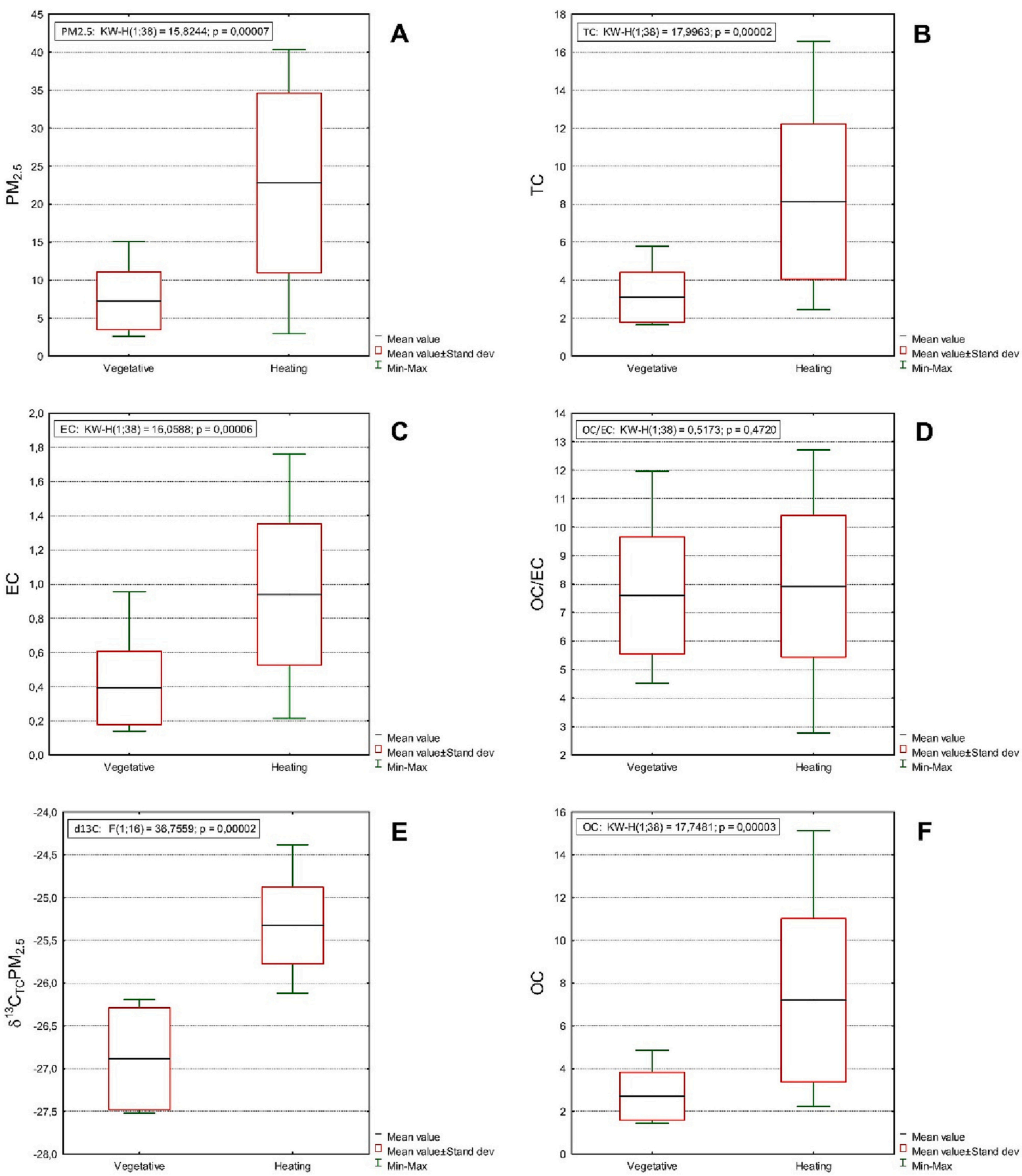

Fig. 4. Box-and-whisker diagrams (mean value/standard deviation and minimum/maximum) for the measured parameters. Samples are discriminated between vegetative and heating seasons. Statistical test by one-way analysis of variance ANOVA was applied for [E] whereas Kruskal–Wallis test by ranks was calculated for [A-D and F].

et al. (2014) attribute this 1630 cm^{-1} peak to an aromatic C═C bond vibration. Zeb et al. (2018) indicated that the presence of C—C aromatic skeletal stretching is indicated by the peak at 1620 cm^{-1} and that PM also contains water, which exhibits absorbance at this wavelength. The signal observed in the region at 1650–1580 cm^{-1} indicates the presence of N—H bending vibrations in amines. It is worth highlighting that $PM_{2.5}$ samples collected in winter yielded two more interesting signals: (i) a strong sharp peak at ~1385 cm^{-1}, which may correspond to NH_4NO_3 (Ji et al., 2014) or cerussite (Usman et al., 2022); (ii) a weaker but still visible peak at 668 cm^{-1} that may indicate the presence of $CaSO_4$ in $PM_{2.5}$ (Zeb et al., 2018). While the ATR method would yield more precise results, the presence of visible peaks in the FTIR spectra still bring useful information (e.g. the C—H stretching vibration in alkanes: 2800–2900 cm^{-1}). Shankar et al. (2022) recently published FTIR spectra representative of $PM_{2.5}$ samples that are similar to ours, not only in the number and wavelengths of the peaks but also in their respective intensities.

Generally, weaker peaks were observed in the $PM_{2.5}$ collected during the vegetative season (04.06.2021 – Fig. 3A) compared to the heating season. Moreover, we observed a lack of signals corresponding to inorganic substances such as ammonium nitrate, cerrusite or calcium sulphate (Fig. 3A). Conversely, slightly more intensive O—H stretching vibrations around 3400 cm^{-1} were observed in vegetative $PM_{2.5}$ compared to the heating season (Fig. 3A). It may indicate the presence of water and/or hydroxylated compounds, such as alcohols and polyols (Acuna-Askar et al., 2022; Siciliano et al., 2018).

Among the other peaks revealed by the FTIR spectra analysis (Fig. 3A and B) those observed in the regions at 1080, 800 and 470 cm^{-1} belong to inorganic materials inherent to the sampling filter, e.g. quartz. Peaks located at ~2350 cm^{-1} are impacted by presence of CO_2 in the sample chamber, hence they are not diagnostic.

3.5. Meteorological/environmental parameters

Average daily meteorological data (air temperature, precipitation amount, relative humidity, wind speed, atmospheric pressure) for the sampling period (01.10.2020–30.09.2021) are reported in Table 1. Daily precipitations and air temperature are presented in Fig. 2. Wind roses for vegetative and heating seasons are shown in Fig. 1. For both sampling periods the dominant wind direction in the studied area was west (36%). During the heating season, periodic episodes blowing from south (18.9%) and east (18.9%) directions were more visible than during the vegetative season (16.5% S and 16.3% E) (Fig. 4A and B). Those directions are typical for the Lower Silesia voivodeship (Dancewicz et al., 2009).

4. Discussion

4.1. Seasonality and sources of pollution

Seasonality in the distribution of air pollutant concentrations in Poland, as well as in Europe, is generally attributed to increased emissions from local sources during winter resulting from a higher demand for home heating combined to specific meteorological conditions: shallow mixing layers and frequent temperature inversions during that period limit pollutant dispersion and removal (Pastuszka et al., 2010; Reizer and Juda-Rezler, 2016). $PM_{2.5}$ concentrations in Legnica displayed statistically significant differences between the heating and vegetative seasons (Kruskal–Wallis test by ranks; Fig. 4A). This trend was also observed for TC, OC and EC concentrations (Fig. 4B, C and F), and carbon isotope compositions (Fig. 4E). It suggests that different $PM_{2.5}$ sources are involved that likely contribute distinctly between the heating and vegetative seasons. Calculated Spearman's correlation coefficients (ρ) with air temperature (−0.60), wind speed (−0.35) and relative humidity (0.44) show that meteorological conditions also play a role in the $PM_{2.5}$ seasonality (Table 2).

OC and EC in $PM_{2.5}$ showed concentrations more than doubled in winter (Fig. 2), which can be interpreted as a result of higher fuel consumption (coal, biomass…) for heating purposes in that cold season of the year (Górka et al., 2020). As previously discussed, two coal-fired heating plants are located in the closest proximity of the study area. However, due to strict controlling regulations regarding their emissions, we hypothesize that their impact may be overprinted by more preponderant emissions such as residential heating or road traffic (Bautista VII et al., 2014; Buch et al., 2021; Cao et al., 2004; Chow et al., 2004; Gu et al., 2010; Watson et al., 1994). Additionnally, the FTIR analysis of the $PM_{2.5}$ samples collected in winter (Fig. 3A and B), supports the conclusion that incomplete combustion of fossil fuels is the most probable source of pollution during that season as it shows the presence of both polycyclic aromatic hydrocarbons (PAHs) and aliphatic hydrocarbons (*n*-alkanes) (Górka et al., 2014). This is comforted by the correlation with $\delta^{13}C$ and TC/OC/EC (Fig. 2). Moreover, the significant amounts of nitrates, ammonia and sulphates present in the winter $PM_{2.5}$ (Fig. 3) can also indicate the influence of solid fuel combustion (coal and lignite). During the vegetative season the presence of water and/or hydroxylated compounds (Fig. 3) may be explained by higher inputs from biogenic sources (Acuna-Askar et al., 2022). This, combined with the observed depletion in ^{13}C in $PM_{2.5}$ (Fig. 2 and Fig. 6) and the high amount of OC_{prim} (~67%), strongly supports the conclusion that biogenic sources contribute to carbonaceous particles during the vegetative season.

OC_{prim} and OC_{sec} concentrations were higher during the heating season: 1.5 and 4.9 times, respectively (Table 1). Generally, favorable meteorological conditions during summer (i.e., higher temperature and insolation) are expected to enhance the formation of OC_{sec}. However,

Table 2
Spearman's correlation coefficients (ρ) between the different parameters measured in the $PM_{2.5}$ samples. The significant correlations ($p < 0.05$) are marked using a bold font. Calculations were made for $n = 38$, except for relations with $\delta^{13}C$ where $n = 18$.

	$PM_{2.5}$ [μg·m^{-3}]	TC [μg·m^{-3}]	OC [μg·m^{-3}]	EC [μg·m^{-3}]	$\delta^{13}C$ [‰]	T [°C]	Precipitation [mm]	Wind speed [m·s^{-1}]	RH [%]	Pressure [hPa]
TC [μg·m^{-3}]	**0.91**									
OC [μg·m^{-3}]	**0.91**	**0.99**								
EC [μg·m^{-3}]	**0.86**	**0.95**	**0.93**							
$\delta^{13}C$ [‰]	**0.89**	**0.94**	**0.92**	**0.73**						
T [°C]	**−0.60**	**−0.62**	**−0.61**	**−0.58**	**−0.83**					
Precipitation [mm]	0.07	0.12	0.10	0.16	0.03	−0.16				
Wind speed [m·s^{-1}]	**−0.35**	**−0.36**	**−0.37**	**−0.34**	−0.04	−0.09	−0.08			
RH [%]	**0.44**	**0.39**	**0.39**	**0.37**	**0.47**	**−0.52**	0.20	−0.29		
Pressure [hPa]	−0.02	−0.09	−0.09	−0.03	−0.22	0.01	−0.16	0.01	0.01	
OC/EC	0.04	−0.04	−0.00	−0.29	0.41	−0.19	−0.22	0.10	0.06	−0.10

during that season specific contaminants (i.e., VOCs from natural (forests, plants, fermentation…) and anthropogenic (e.g. evaporation from fossil fuels) sources) are mostly produced in gaseous form, which may prevent them from transforming into secondary PM (Juda-Rezler et al., 2020). Meanwhile, during winter, the condensation of these gaseous precursors to liquid or solid phase is possible (Błaszczak et al., 2016; Juda-Rezler et al., 2020; Kim et al., 2019; Wang et al., 2019). Studying the sole OC_{prim} and OC_{sec} concentrations in $PM_{2.5}$ thus does not bring unequivocal information regarding the sources of atmospheric carbon species in aerosols, and studies have proposed to also include the study of the OC/EC ratio (eg. in Górka et al., 2020; Tiitta et al., 2014; Vecchi et al., 2004). Factors controlling the OC/EC ratio are the type of emission sources and of fuel that is combusted: a OC/EC < 0.5 corresponds to emissions from diesel (El Haddad et al., 2009; Zielinska et al., 2004), $0.5 <$ OC/EC < 2.5 corresponds to general road traffic (Pio et al., 2011); $2.6 <$ OC/EC < 6.0 to coal combustion for heating purposes (Shen et al., 2010) and OC/EC > 6.0 corresponds to biomass burning (Shen et al., 2010; Tiitta et al., 2014; Watson et al., 2011). Here, results indicate that coal combustion and biomass burning dominated during both seasons whereas road traffic seems to contribute less (Fig. 5). However, it can be noted that the OC/EC ratios yielded slightly larger variations during the heating season (2.8–12.7) compared to the vegetative one (4.5–12.0). It may suggest that more emission sources are involved in winter (i.e. home heating, which is absent in summer). Still, although the respective variances of the OC and EC concentrations were statistically significant (Fig. 4C and F), a Kruskal–Wallis test showed that the seasonal variations of the OC/EC ratio are not (Fig. 4D). Thus, we conclude that the OC/EC ratio should not be used as a single proxy when tracking the origin of the carbonaceous PM fraction without conducting adequate statistical tests. Moreover, we highly recommend the use of the OC/EC ratio coupled with other parameters of the carbonaceous phases (eg. isotopes or molecular analysis), as presented in this study. Such a multi-proxy analysis is required to avoid misinterpretation on the origin of PM.

Authors have proposed to use isotope mass balance (IMB) modeling to better understand seasonal differences in the potential origins of carbonaceous PM (Górka et al., 2020; Górka et al., 2014). The approach is based on the hypothesis that the $\delta^{13}C$ of PM tends towards the isotope composition of the corresponding emission source(s) when its TC concentration becomes very large compared to that of the background aerosol mass (Górka et al., 2020). Here we used the $\delta^{13}C$ value of −27.5‰, reported by Górka and Jędrysek (2008), for road traffic, that represents equal contributions from diesel and gasoline vehicles. The same authors defined a $\delta^{13}C$ of −24.5‰ for coal burning. These were the two endmembers we considered for the heating season. For the vegetative season a supplementary source, representing total biogenic sources, was added to the calculation, for which an isotope composition of −29.3‰ was attributed (Górka and Jędrysek, 2008). Similarly to the results obtained in Lower Silesia by Górka et al. (2020) for the coarse (PM_{10}) fraction (average $\delta^{13}C$ of −27.0‰ for the heating season and −25.0 ‰ for the vegetative season), we also observed here a clear discrimination for the fine fraction ($PM_{2.5}$) between the heating and vegetative seasons (average $\delta^{13}C$ of −26.3 and − 24.1‰, respectively; Fig. 6). This ~1‰ enrichment in ^{13}C between the PM_{10} and $PM_{2.5}$ fractions may be attributed to various factors, including a shift in the respective contributions of the emissions sources between the two sampling campaigns (PM samples collected 10-years apart). Results from the IMB calculation yielded the following contributions in our $PM_{2.5}$ samples: (i) heating season: 95% coal combustion and 5% road traffic, and (ii) vegetative season: 52% coal combustion, 12% road traffic and 38% biomass burning. These contributions are distinct from those obtained in 2011 in Lower Silesia for PM_{10} with 60% for coal combustion and 40% for road traffic during the heating season, and 22% for coal combustion, 74% for road traffic and 4% for biomass burning (Górka et al., 2020). This increase in the contribution from coal combustion may be explained by: (i) C-rich fine aerosols from coal combustion whose origin is from outside of the Legnica; (ii) the influence of the Legnica smelter that combusts coke for non-ferrous metal production. Górka et al. (2020) excluded the high chimneys of the smelter as a possible source of aerosol contamination for PM_{10} in their conclusions. Still, Bartz et al. (2021), in his study of the smelter of Głogów (50 km north of Legnica), demonstrated that significant amounts of ultrafine and fine anthropogenic aerosols can be detected near a smelter. Except for episodic unfavorable wind conditions, the impact of emissions from home heating from the center of Legnica may be considered negligible at

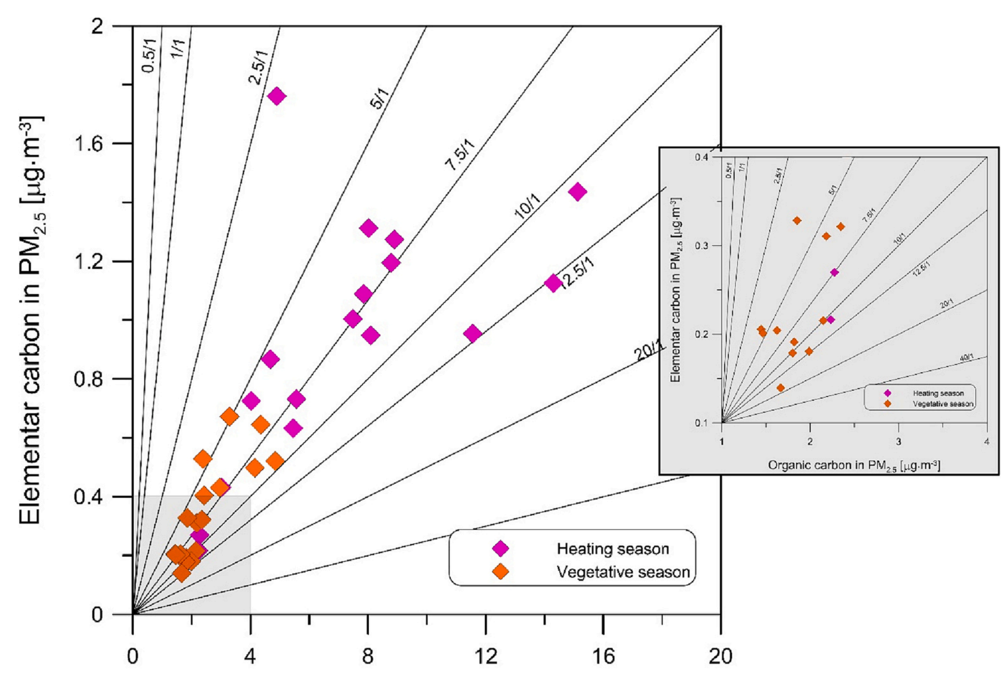

Fig. 5. OC/EC ratio measured in $PM_{2.5}$ samples during the heating and vegetative seasons.

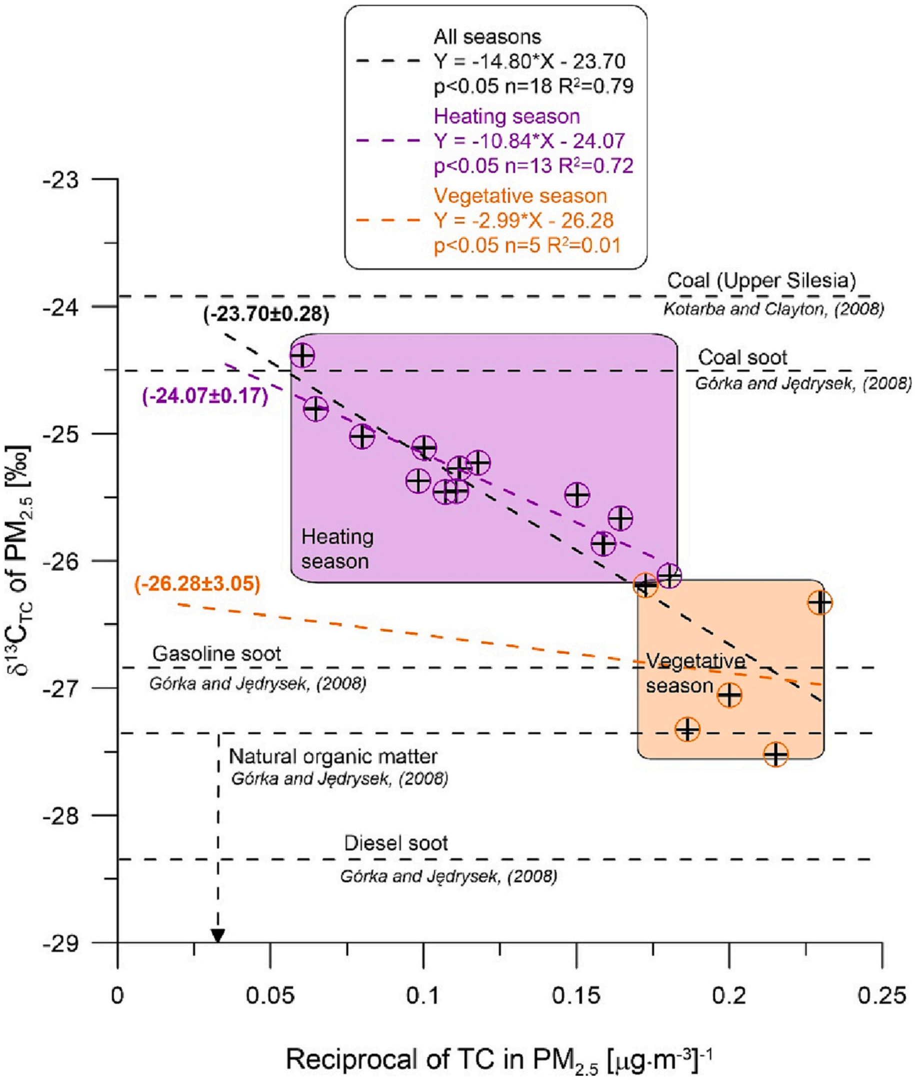

Fig. 6. Relationship between the reciprocal concentration of TC in $PM_{2.5}$ and its $\delta^{13}C$ composition in Legnica during a one-year measuring campaign. Typical gasoline, diesel and coal soot, as well as natural organic matter carbon isotopes compositions are from Górka and Jędrysek (2008). Coal isotope composition is from Kotarba and Clayton (2003).

our sampling location, due to the predominant W-direction winds (Fig. 1). However, due to small number of $\delta^{13}C$ values obtained for the vegetative season and the high standard error ($\pm$3.05 ‰) associated to the $\delta^{13}C$ value of the corresponding intercept (Fig. 6), we did not consider the results of the IMB calculation for the vegetative season.

4.2. Seasonal episodes

As proposed by Chen et al. (2020) we conducted additional daily samplings for a period of one-week both in winter (06–12.02.2021) and summer (14–20.08.2021), in order to better understand the seasonal influence of meteorological conditions on $PM_{2.5}$ and its components concentrations as well as the potential interactions between. As stated by the authors this approach at a smaller time scale is expected to allow for a better seasonal interpretation of the origin of emission sources as meteorological conditions (rapid changes in temperature, wind, and pressure), caused by a frontal system, may significantly influence air pollution conditions (Chen et al., 2020).

4.2.1. Winter (06–12.02.2021) episode

$PM_{2.5}$ concentrations are affected by multiple meteorological factors (Chen et al., 2020). During the winter 2020/2021 episode, $PM_{2.5}$ concentration increased from 21.4 $\mu g \cdot m^{-3}$ (06.02.2021) to 40.3 $\mu g \cdot m^{-3}$ (09.02.2021) (Fig. 8 and Table 1). This is in agreement with the increase observed at CIEP Legnica station for the same period (Table 1), even if the increase is more pronounced at the station (from 19.6 to 52.5 $\mu g \cdot m^{-3}$). Fig. 7 and 9 show the concomitant formation of three low-pressure systems in Europe on 10.02.2021 coupled to a high-pressure system over the Scandinavian region that caused cold advection from north and northeast directions (see HYSPLIT trajectory in Fig. 7A, Fig. 7B). This caused a shift into local air masses that moved from the center of Legnica southwards the sampling location, opposite of the typical dominant west wind direction. Moreover, during the central 2-days of the episode the pressure gradient weakened, and wind speed decreased down to 0 $m \cdot s^{-1}$. Stable atmospheric boundary layer inhibited the pollutant dispersion, resulting in high $PM_{2.5}$ concentrations (He et al., 2017). During that episode, air pressure dropped from 1003 hPa to 987 hPa, and air temperature decreased from −1 °C to −9 °C (Table 1 and Fig. 8). Low temperatures weaken atmospheric convection and enhance the accumulation of $PM_{2.5}$ (Chen et al., 2020; Li et al., 2014, 2015). Relative humidity (RH) increased from 73% to 84% with snow events recorded during the first 4 days of the episode (Table 1). A higher RH affects $PM_{2.5}$ concentrations as a higher vapor content (i) increases hygroscopy, leading to higher accumulation of $PM_{2.5}$ (Chen et al., 2020);

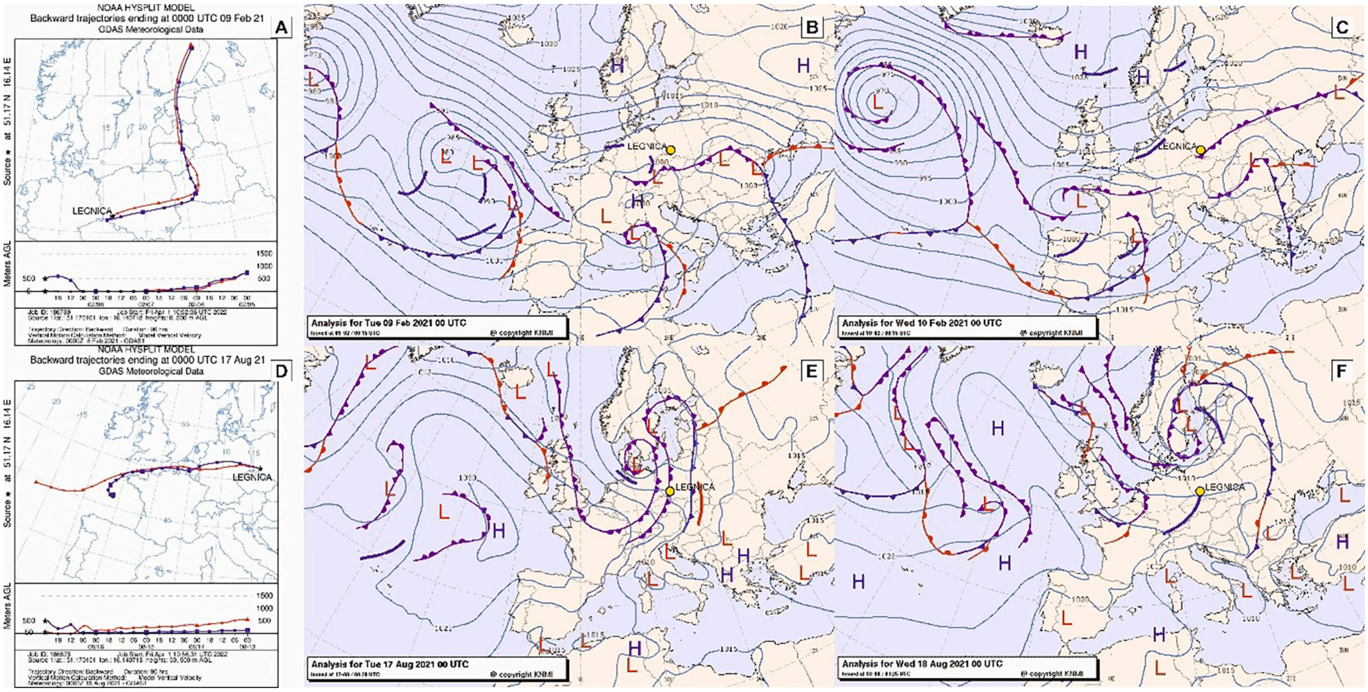

Fig. 7. HYSPLIT backward trajectories in Legnica calculated for [A] winter (09.02.2021) and [D] summer (17.08.2021) episodes. KNMI synoptic charts (https://www.knmi.nl, accessed on 1 April 2022) corresponding to the fourth SOM-based weather patterns at 00:00 UTC on [B] 09.02.2021 and [C) 10.02.2021 winter episode and [E] 17.08.2021 and [F] 18.08.2021. The prominent synoptic features are shown: L (low pressure), H (high pressure), blue (cold front), red (warm front) and magenta (occluded front). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

(ii) favors gas-to particle conversion, increasing the fraction of hygroscopic components, especially ammonium nitrate, which further increases water uptake and $PM_{2.5}$ mass concentration (Chen et al., 2020). FTIR analysis of our $PM_{2.5}$ collected during that winter episode confirmed the presence of an intensive ammonium peak existed (Fig. 3B). Although Tian et al. (2021) demonstrated that snow events may decrease $PM_{2.5}$ concentrations by an average of 26%, we did not observe such trend (Fig. 7). Ultimately, unfavorable meteorological conditions, leading to highly polluted air masses being transported from the center of Legnica towards our sampling station, caused an significant peak in the $PM_{2.5}$ concentrations. The corresponding enrichment in ^{13}C we observed in $PM_{2.5}$ samples (average $\delta^{13}C$ of $-25.24 \pm 0.2‰$) indicates that coal combustion was the main vector of the carbonaceous air pollution (Fig. 8).

4.2.2. *Summer (14–21.08.2021) episode*

During the summer episode, $PM_{2.5}$ concentrations decreased from 11.4 $\mu g \cdot m^{-3}$ (14.08.2021) to 3.9 $\mu g \cdot m^{-3}$ (18.08.2021) (Fig. 9 and Table 1), similar again to what was observed at the CIEP Legnica station (from 17.1 $\mu g \cdot m^{-3}$ to 6.3 $\mu g \cdot m^{-3}$; Table 1). During that period the weather was affected by low-pressure systems that had developed over the northern part of Europe and the frontal zones that were associated to them (Fig. 7E-F and Fig. 9). A zonal west circulation, slightly disturbed by the Azores highs, predominated over Poland that was confirmed by HYSPLIT trajectory (Fig. 7D). Wind speed was relatively high, with a maximum of 5.4 $m \cdot s^{-1}$. Generally, high velocity wind and an unstable atmosphere favor $PM_{2.5}$ dispersion (Chen et al., 2020; Zhang et al., 2017). Wind speed plays a crucial role in the evaporation loss rate of $PM_{2.5}$ (Chen et al., 2020; Han et al., 2018) and indirectly reduce $PM_{2.5}$ mass concentration. During this summer episode air pressure slightly fluctuated, from 1004 to 994 hPa (Table 1 and Fig. 8), finally stabilizing at ~1000 hPa for the last four days. During the first 3 days of the episode (14–16.08.2021) temperatures reached 30 °C, with a daily average of ~22 °C (Table 1 and Fig. 9). This was followed by a few cold days (17–18.08.2021) before the average temperature rose again. These high temperatures resulted in more intense thermal turbulences, accelerating $PM_{2.5}$ dispersion (Chen et al., 2020; Yang et al., 2016). Similarly to high wind velocity, high temperatures lead to an increased evaporation rate and thus to $PM_{2.5}$ mass loss (Chen et al., 2020), including the loss of water vapor, of ammonium nitrate and of other volatile or semi-volatile components (Wang et al., 2006). This was confirmed by the FTIR analysis (Fig. 3B) that showed the absence of an ammonium peak. In addition the amount of $OC_{sec,}$ which can result of VOCs conversion, was low compared to the winter episode (Table 1). RH was relatively low (between 63 and 69%), except for the last day of the episode where it increased to 76%. Lower RH likely help increase the $PM_{2.5}$ evaporation loss (Chen et al., 2020) as this process is opposed to the hygroscopic one that increases the $PM_{2.5}$ mass concentration.

In summary, the low $PM_{2.5}$ concentrations in summer may be interpreted as a result of favorable meteorological conditions (high wind speed and temperatures and low RH), which allowed to remove directly and indirectly $PM_{2.5}$ (and its pollutants) from the atmosphere. It can also be noted that lower inputs from natural and anthropogenic PM are expected during that period compared to winter.

5. Conclusions

Our study strongly recommends that a multi-proxy approach is implemented to provide a reliable assessment of air quality and of the corresponding sources of $PM_{2.5}$ and to avoid pitfalls in the data interpretation. The study of $PM_{2.5}$ collected in the vicinity of Legnica (Lower Silesia) water treatment plant, conducted in 2020 and 2021, indicated that:

(i) $PM_{2.5}$ concentrations measured at our monitoring station agree with those obtained at the (CIEP) station in Legnica.
(ii) statistically significant seasonal differences were observed for $PM_{2.5}$, TC, OC and EC concentrations, carbon isotope compositions ($\delta^{13}C_{TC}$) and FTIR spectra.

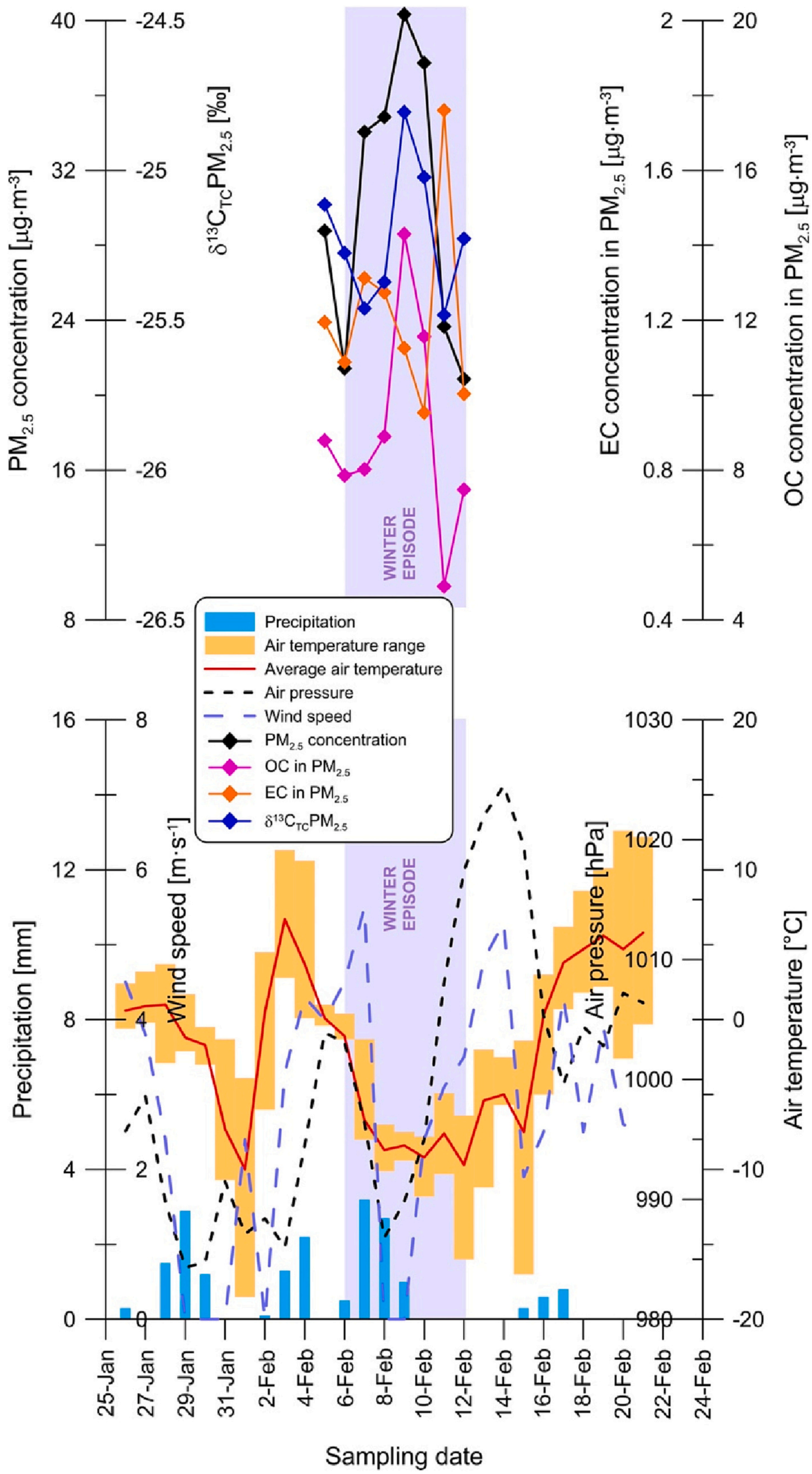

Fig. 8. Temporal variations of the geochemical ($PM_{2.5}$, TC, OC, EC and $\delta^{13}C_{TC}$) and meteorological (min/max/average temperature and precipitation) parameters during the winter episode (06–12.02.2021).

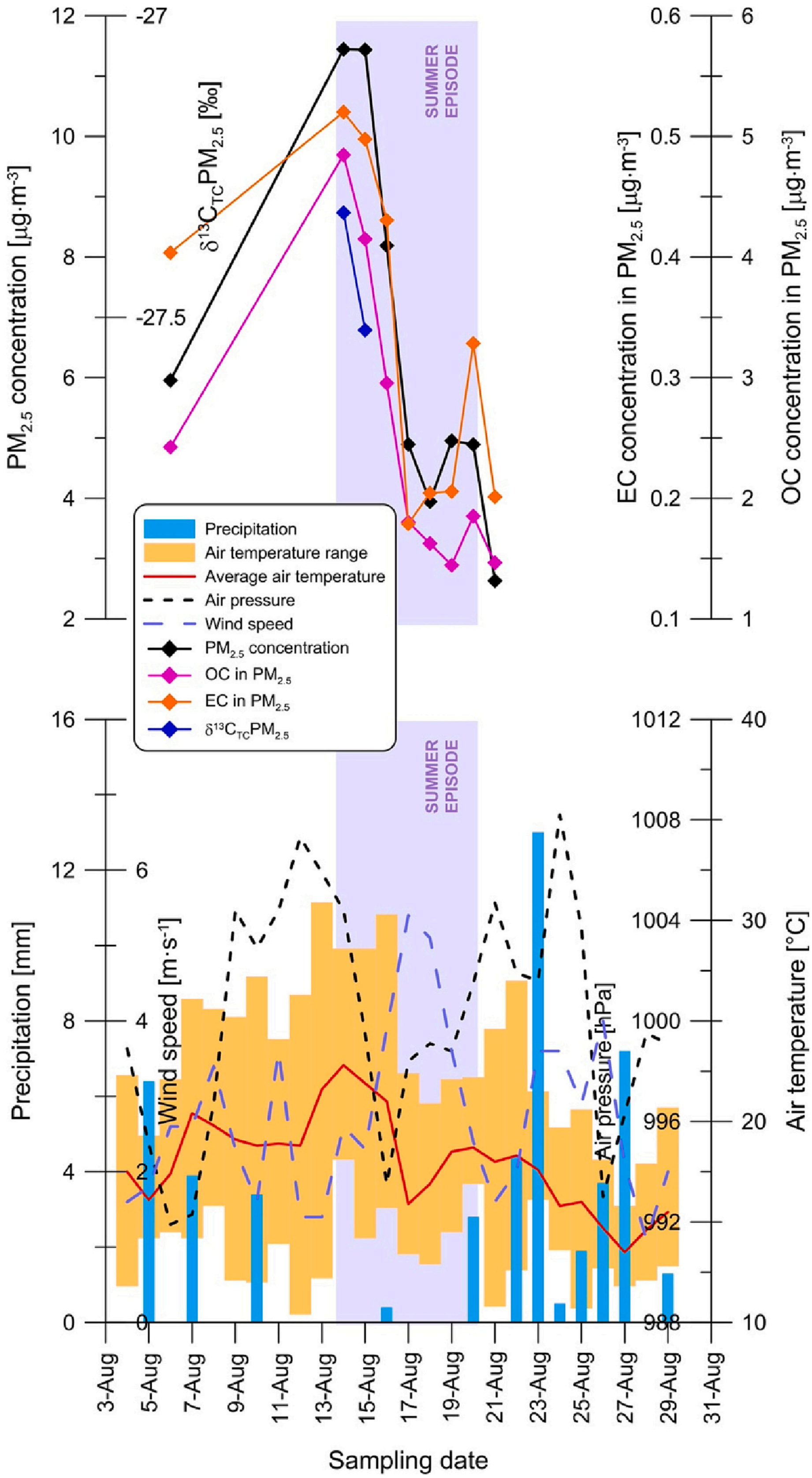

Fig. 9. Temporal variations of the geochemical ($PM_{2.5}$, TC, OC, EC and $\delta^{13}C_{TC}$) and meteorological (min/max/average temperature and precipitation) parameters during the summer episode (14–20.08.2021).

(iii) calculated OC_{prim} and OC_{sec} concentrations also confirmed a strong seasonal variability. While OC_{sec} dominated in winter, OC_{prim} contributed more to the OC total mass in summer, which indicated differences in the relative shares of PM emissions between the two seasons.
(iv) If used as a single proxy, the commonly used OC/EC ratio may lead to an incorrect interpretation of the origin of the carbonaceous PM fraction.
(v) Using an isotope mass balance (IMB) model, we identified that the main source of pollution in winter was coal combustion whereas in summer it was a mixture of aerosols from coal combustion, road traffic and bio/organic burning. However, we decided not to consider that results from the IMB model due to the insufficient number of samples analyzed.
(vi) the added value of coupling multiple proxies, TC/OC/EC, $\delta^{13}C$ and FTIR, showed in the possibility to precisely identify the sources of the carbonaceous compounds present in $PM_{2.5}$: while coal combustion and road traffic dominated during the winter/heating season, biomass burning and road traffic did during the summer/vegetative season.

Additionally, based on the study of two 7-day episodes (one in summer and one in winter) we concluded that meteorological conditions strongly influence $PM_{2.5}$ concentration, favoring high concentrations episodes in winter attributed to the increased activity of local home heating. In summer lower $PM_{2.5}$ concentrations were resulting from favorable meteorological conditions that led to the direct and indirect removing of air pollution.

The study showed how important it is to conduct a complex PM analysis and to consider all collected data altogether in order to avoid misinterpretation. A comprehensive analysis of the sources of PMx pollution is thus expected to help designing and implementing remediation plans aimed at improving air quality in Poland and to a larger extent in Europe.

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CRediT authorship contribution statement

Maciej Górka: Conceptualization, Formal analysis, Investigation, Methodology, Project administration, Resources, Writing – original draft, Visualization, Supervision. **Agnieszka Trzyna:** Conceptualization, Investigation, Methodology, Funding acquisition, Project administration, Writing – original draft. **Anita Lewandowska:** Investigation, Methodology, Resources, Validation, Writing – original draft. **Anetta Drzeniecka-Osiadacz:** Resources, Funding acquisition, Writing – review & editing. **Beata Miazga:** Investigation, Methodology, Resources, Visualization, Writing – original draft. **Justyna Rybak:** Project administration, Funding acquisition, Writing – review & editing. **David Widory:** Writing – review & editing, Supervision.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

Data will be made available on request.

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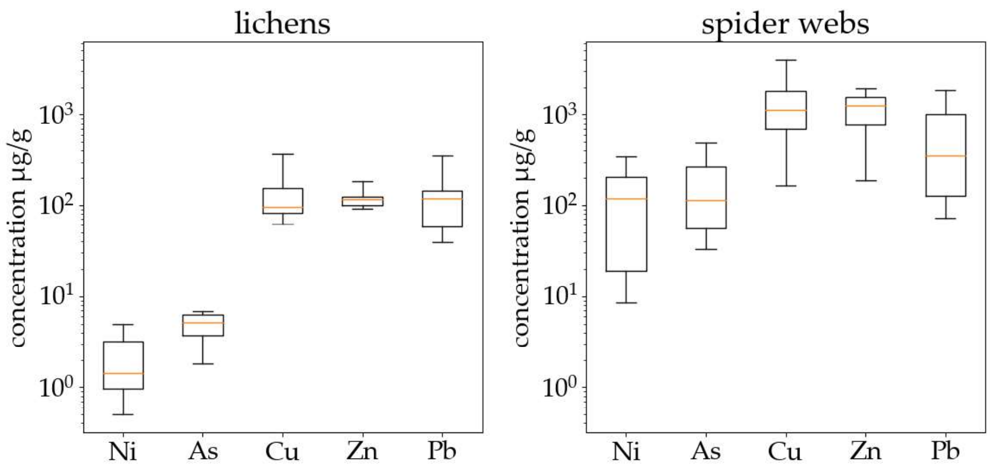
Artykuł 3

Porównanie kumulacji pierwiastków potencjalnie toksycznych przez sieci pajęcze oraz porosty

Spider webs and lichens as bioindicators of heavy metals: a comparison study in the vicinity of a copper smelter (Poland). **Agnieszka Stojanowska**, Justyna Rybak, Marta Bożym, Tomasz Olszowski, Jan Stefan Bihałowicz. *Sustainability*. 2020, vol. 12, nr 19, art. 8066, s. 1-13.

Celem poniższej pracy było ilościowe porównanie zanieczyszczeń akumulowanych przez dwa różne bioindykatory: sieci pajęcze i porosty. Badania te motywował fakt, że pomimo coraz częstszego wykorzystywania sieci pajęczych w biomonitoringu powietrza, taki eksperyment nie został nigdy wcześniej przeprowadzony. Biorąc pod uwagę powszechność wykorzystywania porostów w badaniach dotyczących jakości powietrza bioindykator ten został uznany jako najbardziej odpowiedni do wykonania pierwszej analizy porównawczej w stosunku do rzadziej używanych sieci pajęczych.

Eksperyment przeprowadzono na terenie miasta Legnicy, gdzie wybrano dziesięć stanowisk badawczych położonych w niedalekiej odległości od huty miedzi Legnica. W badaniu wykorzystano transplantowane czyste sieci pajęcze pająków z rodziny Agelenidae oraz transplantowane porosty - *Hypogymnia physodes* (L.), czyli pustułkę pęcherzykowatą. Po dwumiesięcznym czasie ekspozycji w bioindykatorach oznaczono następujące pierwiastki potencjalnie toksyczne: Cu, Zn, Ni, Pb oraz As. Wyniki wykazały, że pomimo identycznego czasu ekspozycji, sieci pajęcze zakumulowały znacznie większe ilości wybranych pierwiastków niż porosty, niekiedy nawet więcej o rząd wielkości (Rysunek 2), a różnice te były statystycznie istotne.



Rysunek 2 Stężenia pierwiastków w plechach porostów i na sieciach pajęczych (µg/g; Stojanowska et al. 2020).

Otrzymane wyniki są niezwykle ciekawe, ale i zastanawiające, dlaczego sieci pajęcze mają tak dużą przewagę w ilości akumulowanych zanieczyszczeń. Jednym z wytłumaczeń tej sytuacji może być fakt, że porosty posiadają punkt wysycenia, w którym dalsze akumulowanie pierwiastków jest niemożliwe, natomiast w przypadku sieci pajęczych taka sytuacja nie jest znana. Co więcej, sieci pajęcze, w przeciwieństwie do porostów, nie wykazują wrażliwości na zanieczyszczenia, stąd nie posiadają żadnych ograniczeń w stosowaniu nawet na silnie zanieczyszczonych obszarach. Powyższe rozważanie prowadzić może do wniosku, że sieci pajęcze są bardziej efektywnym bioindykatorem niż powszechnie stosowane porosty.

Pomimo wyżej wspomnianych różnic w bezpośrednim porównaniu ilości akumulowanych zanieczyszczeń, szereg stężeń pierwiastków uporządkowanych malejąco był właściwie taki sam, co daje zgodną informację co do głównego źródła zanieczyszczeń na badanym obszarze. Oba bioindykatory wskazały na znaczącą rolę huty miedzi w zanieczyszczeniu powietrza w Legnicy, a dodatkowo do tej sytuacji mogła przyczyniać się obecność ruchliwych dróg w okolicy. Co więcej, obliczenie współczynnika zanieczyszczenia (CF, z, ang. contamination factor) pozwoliło na wyciągnięcie wniosków, że zanieczyszczenie Ni oraz Zn na tym terenie może zostać uznane za niewielkie, natomiast w przypadku Cu oraz Pb sytuacja jest dużo poważniejsza, gdyż współczynnik CF wskazał odpowiednio na silne oraz ekstremalnie silnie zanieczyszczenie. Wyniki te potwierdziły więc przypuszczenia co do głównych źródeł zanieczyszczeń na tym obszarze.

Wniosek: Sieci pajęcze akumulują dużo wyższe ilości zanieczyszczeń niż porosty, jednak odpowiedź obu bioindykatorów na temat głównego źródła zanieczyszczeń na badanym obszarze jest zgodna.

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Spider Webs and Lichens as Bioindicators of Heavy Metals: A Comparison Study in the Vicinity of a Copper Smelter (Poland)

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Abstract: This paper presents the comparison of heavy metals accumulation in spider webs from Agelenidae family (*Eratigena atrica* and *Agelena labyrinthica*) and lichens *Hypogymnia physodes*, exposed to pollution for two months. Webs were obtained from the laboratory-reared spiders and stretched on Petri dish while lichens were transplanted from Stobrawa Landscape Park into the study area. Concentrations of Cu, Zn, Ni, Pb and As were determined in both biomonitors and the elevated values indicated the impact of the copper smelter and surrounding roads. Our study revealed that webs were more sensitive than lichens to emissions of pollutants, and for all of the studied elements, the determined concentrations were much higher for spider webs. The results of similarity tests showed a clear difference among the concentrations of Cu, Zn, Ni and As in lichens and spider webs, with the exception of Pb, suggesting that this element could be accumulated in a similar way by both bioindicators. These differences are probably due to their morphological and ecological dissimilarities suggesting that spider webs should be favorably applied where the use of lichens is improper due to the drought, which is an unfavorable condition for accumulation of elements in lichens, or their limited uptake of elements.

Keywords: biomonitoring; heavy metals; lichens; spider webs

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1. Introduction

Biomonitoring of air pollutants with the application of lichens has become very popular over the years [1]. Lichens are an especially good tool for this purpose as they do not have a well-developed cuticle, and they also do not have roots that are able to absorb water and minerals since they are strictly dependent on atmospheric deposition [2]. Lichens have been successfully used for more than 30 years for the assessment of the atmospheric deposition of heavy metals in different areas [3,4].

In industrial or urban sites, the lichens occur rarely or are even absent, therefore the "bags technique" was developed and successfully applied [5]. Bags usually contain nylon mesh with water-washed lichens. The following advantages of this method are underlined: the exactly defined entrapment surface and time of exposure, the possibility of site selection, the defined initial concentrations of pollutants in lichens and general greater efficiency of samples collection, the exclusion of possible contamination deriving from root uptake, which is probable when we use dust fall jars or bulk samplers; and finally, this method is cheap and effective [3]. The biggest drawback of the bag method is that the collection efficiency for various contaminants is not defined. This was studied for mosses [6]. The authors suggest that data reflects relative rates of deposition but cannot be applied as the total atmospheric load of contaminants. Garty et al. [7] indicated another problem connected with applying this matrix, as it could reach a saturation point for the uptake of studied metal, thus, the further accumulation is not possible. Climate and other environmental conditions may also influence the results of biomonitoring with lichens.

On the other hand, spider webs are a quite new tool and they are not as commonly used as other bioindicators, although they are present almost everywhere [8–12]. Unlike lichens, they are common in the natural environment as well as in industrialized urban areas. Webs accumulate pollutants efficiently, therefore they are an excellent source of information on the environment quality.

The major advantages of webs' application are: common availability of webs, very convenient location (they are usually woven in secluded places) preventing them from being destroyed by weather conditions (rain, wind etc.), low cost, easy samples' collection and non-invasiveness of studies. Webs are also a non-specific and universal tool as they do not need any preparation before sampling. They are organic, natural and environment-friendly products which do not need to be degraded (no waste production, e.g., used sorbents). Furthermore, spiders can be bred under laboratory conditions and obtained webs can be also used in any place in the same way as lichens or moss bags. Finally, it is also possible to define the exposure time by removing the old web and using only a new construction, or by applying the web obtained in the laboratory.

However, no investigations have focused on the comparison of the accumulation capacity of the two types of organisms so far. Therefore, the aim of our study was to compare these two bioindicators to assess their efficiency and relevance for the bioindication purposes. To accomplish this aim, we determined the selected metals in the vicinity of a copper smelter, which is known for its impact on the air and soil pollution in the studied region.

2. Materials and Methods

2.1. Study Area

The research was carried out in Legnica, western Poland (Figure 1), where a copper smelter and refinery (KGHM) is located. This smelter is known to have an adverse effect on the environment, i.e., air [13] as well as on the soil, in which a high proportion of anthropogenic lead can be noted [14]. Its tasks include many operations, from mining to the manufacture of fabricated metal products. The main products of KGHM are electrolytic copper in the form of cathodes and refined silver and lead. The smelter was opened in 1953 and at the beginning, it emitted fly ash materials, containing large amounts of metals. In the 1980s and 1990s, the emission was significantly reduced [15]. Additionally, between 1995 and 2000, some serious steps were undertaken, and in 2000, the total dust emission was 96.6% smaller comparing to 1995 [13]. Despite this, nowadays, there can be found high amounts of hazardous substances in the studied area. In the Information On Air Quality In The Area Of Legnica City [16], presented by Provincial Inspectorate for Environmental Protection (WIOS), high levels of arsenic were determined when analyzing PM_{10} particles. What is more, high levels of polycyclic aromatic hydrocarbons (PAHs) were found in the air. The measured mean annual concentration of benzo(a)pyrene was 603% of the target level. According to the Provincial Inspectorate for Environmental Protection report [16] measured lead concentrations decreased by 38%, cadmium by 52% and nickel by 35% when comparing to results from 2005. An increase was observed when analyzing arsenic levels. Compared to 2005, its concentration enlarged by 127% [16].

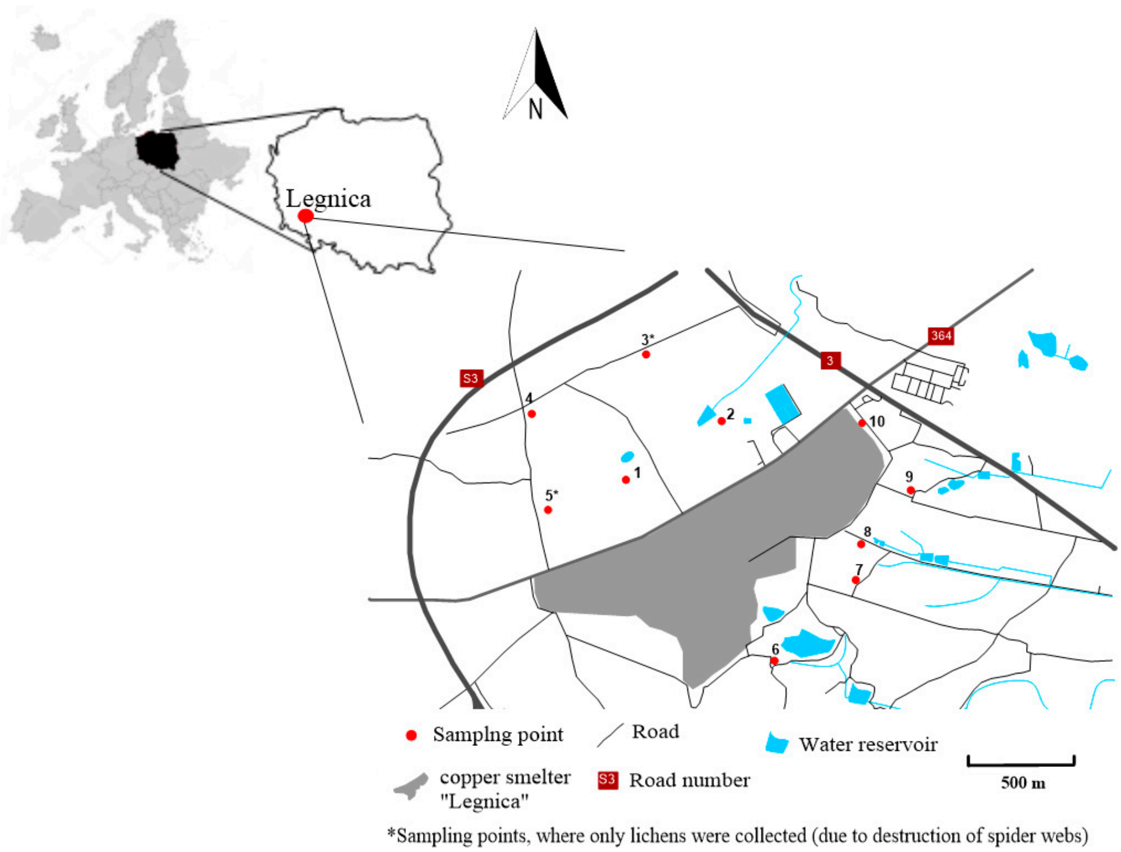

Figure 1. Localization of study area and sampling points in the vicinity of copper smelter "Legnica".

2.2. Materials and Methods

In this study, the transplantation method of lichens and spider webs was performed. The epiphytic lichen *Hypogymnia physodes* (L.) was chosen as a bioindicator of air pollution studies. This lichen is commonly applied when assessing air quality in Poland [17–19], Russia [20], Slovenia [21], and Republic of Macedonia [22] which indicates its usefulness.

Control lichens were collected in Stobrawa Landscape Park (Stobrawski Park Krajobrazowy) and then transplanted for 2 months (August to October 2019) to 10 study sites (SM Table S1), distributed around "Legnica" copper smelter in Legnica (Figure 1). Element content in control lichens samples, performed preliminary, were as follows: 5 ± 1.4 µg/g for Cu, 45 ± 15.5 µg/g for Zn, 1.2 ± 0.53 µg/g for Ni, 9 ± 2.7 µg/g for Pb, 0.2 ± 0.04 µg/g for As. About six branches with lichens, ca. 15 cm long each, were tied up with a fishing line and hung in each sampling point on trees at a height of 1.5 m. After the exposition, lichens were collected, separated from bark of branches and stored in paper bags, pending further investigation. Then, the thalli samples were homogenized. The 0.1 g of each sample was mineralized in 65% HNO_3 Sigma Aldrich Suprapur using Velp DKL 8 (digestion for 10 min at 100 °C and then for 50 min at 120 °C) in order to acquire total concentrations of metals. Obtained solutions were filtrated and filled up to 10 mL with ultrapure water in glass volumetric flasks and analyzed with the methods described below.

Spider webs of the Agelenidae family (*Eratigena atrica* (C.L. KOCH, 1843), *Agelena labyrinthica* (CLERCK, 1757)) were used for this study. Webs woven by these spiders are characterized by a horizontal flat sheet, built from irregular dense threads, and a funnel-shaped tunnel where the spider hides [23]. The specific construction of the web makes it a good trap for air pollution, even though the webs woven by these spiders are not sticky. Spiders from this family occur in dark corners in houses, basements, as well as in grasses and low bushes. What is more, they can be easily bred in laboratory conditions. Agelenidae do not have the habit of eating their own web [24], which is an important feature, allowing to obtain clean spider web and using it for transplantation in the studied area. Webs of other Agelenids can be also used in such studies [10,11].

To avoid uncontrolled contamination of webs by metals built in the threads, we used webs obtained from laboratory-bred spiders. Samples of already woven webs were stretched over Petri dishes and left for continuous exposure to pollutants in the same locations as lichens, attached with Petri dishes to the branches of trees (SM Table S1). After approximately two months of exposition, all webs were collected using glass baguettes and stored in sterile glass vials pending further analyses. The preliminary concentrations (pre-exposure) for webs produced by spiders in laboratory was previously checked and revealed the absence of studied metals. Samples were conditioned for 24 h at 20 °C and 50% relative humidity and then weighed two times using analytical balance Radwag AS 60/C/2 (accuracy 10-5 g, at a temperature of 23 ± 2 °C and relative humidity of 40 ± 5%). Each sample was mineralized in 65% HNO3 Merck Millipore Suprapur using Velp DKL 8 (digestion for 10 min at 100 °C and then for 50 min at 120 °C). Obtained solutions were filtrated using hard filters and filled up to 10 mL with ultrapure water in glass volumetric flasks and analyzed with the methods described below.

The analyses of mineralized samples were performed at the Department of Environmental Engineering, Opole University of Technology. Cu, Zn, Ni and Pb levels were determined in the solutions in three replications using Flame Atomic Absorption Spectrometry (FAAS) method, while the concentration of As was measured using Hydride Generation Atomic Absorption Spectrophotometry (HG-AAS) technique. The analyses were conducted with the use of spectrophotometer Solaar 6M Thermo. The concentration of metals at studied sites was calculated as the arithmetic mean of three independent samples. Quality check for metals and As analyses were performed with Merck standards in 0.1M HNO_3 (Merck). Blank samples were usually below the detection limit. Certified reference materials (CRM 482) were used for metal content determination in the samples and the accuracy of digestion and analytical procedures. The recovery of CRM ranged from 90 to 107%.

Surfer 10.0 was used to construct Figure 1 by using Kriging method, which is recommended and considered as one of the most flexible and accurate methods.

2.3. Contamination Factor

In order to assess the level of contamination in the studied area, contamination factor (CF) was calculated. This index is presented as the ratio of the concentration of elements in lichens in the study area to the level of the same elements in the control, not contaminated, area. Considering the paper by Koroleva and Revunkov [20], in which the results were compared with the samples from uncontaminated area, we used the levels estimated by Darnajoux et al. [25] as background, as the lichens studied by them were taken from a pristine area with the negligible human influence.

To interpret the results, six categories of contamination factor values were introduced in Table 1 [20,26].

Table 1. Categories of contamination factor.

C1	CF < 1	no contamination
C2	1 < CF < 2	suspected contamination
C3	2 < CF < 3.5	slight contamination
C4	3.5 < CF < 8	moderate contamination
C5	8 < CF < 27	severe contamination
C6	CF > 27	extreme contamination

2.4. Statistics

Firstly, the data were described using descriptive statistics measures. In order to decide whether parametric or non-parametric statistics methods should be applied, the Shapiro–Wilk test [27] was used as the test with the highest power [28]. The null hypothesis was that the collected data are normally distributed and $p < 0.01$. Since all the concentrations are positive numbers, there was an idea to log-transform data if the null hypothesis should be rejected, however, Feng et al. [29] showed that the conclusions drawn from testing log-transformed data do not have to be relevant for the original data set. Considering this, if the result of the Shapiro–Wilk test indicated rejecting the null hypothesis, a non-parametric test would be used for these series. Otherwise, a parametric test would be used.

Then, the lichens and spider webs' concentration of given metal were checked whether both have the same average value or not. Depending on the normality, the Welch's t-test [30] was used for the samples which were normal and the Wilcoxon signed-rank test was used for [31] the others. For both tests, $p < 0.05$ was used, with the null hypothesis that lichens and spider webs reveal equality of average values. Since the sample size was small, the critical values for the Wilcoxon signed-rank test were taken from tables [32].

The concentration of the metals was also compared between lichens and spider webs at the given sites. To do this, a cosine similarity was used, which is, in fact, the inner product of two vectors of the same dimension divided by the product of their lengths [33]. The vector of concentrations measured on the lichens for a given site was compared with the vector of concentrations on the spider webs for the same site.

All statistical calculations were done using Python 3.7 with the packages of pandas [34], SciPy [35], Matplotlib [36].

2.5. Meteorological/Environmental Parameters

In general, the year 2019 was extremely hot, with the annual average temperature equal to 10.2 °C. During studies, the monthly average temperatures amounted to 21.2 °C, 15.2 °C and 11.5 °C in August, September and October, respectively. In the terms of precipitation, the year was considered dry. In the study area, west or south-west winds dominate while the north-east winds have the smallest share [37,38].

3. Results

The concentration of five elements (Cu, Zn, Ni, Pb, As) was assessed in lichens and spider webs (Figure 2). Analyzed samples revealed varying concentrations of considered metals, with generally higher results for all elements at spider webs.

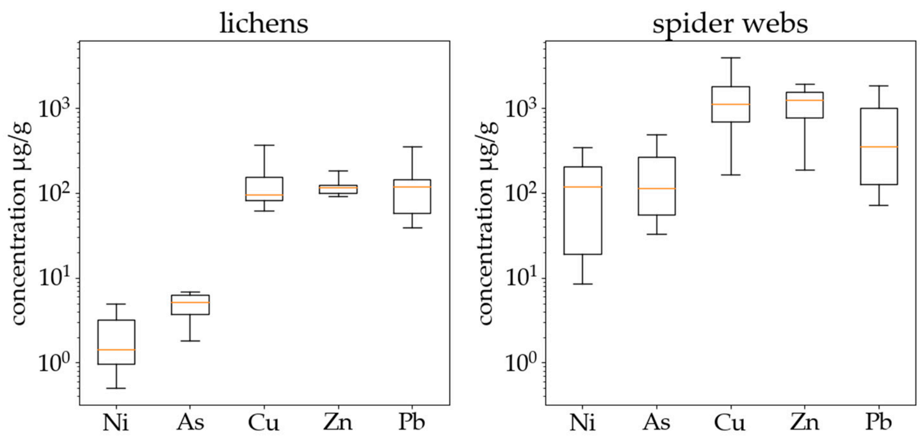

Figure 2. Element concentrations in the *H. physodes* thallus and on spider webs (µg/g). In the plot, the box represents the interquartile range, whiskers are from the minimum to maximum value, and the median is marked with an orange line.

Comparison of median values shows that the most accumulated element in webs was Zn, then in descending order, Cu > Pb > Ni > As. The similar order was established for lichens. The highest values were obtained for Pb, then Zn > Cu > As > Ni (Figure 2). Median values differed significantly between these two bioindicators but Figure 2 shows that Cu, Zn and Pb were established at higher levels when comparing to As and Ni in lichens and spider webs as well. When comparing the median mass of heavy metals on spider webs and lichens, we noticed that for each element, the accumulation on spider webs was greater than in lichens (Figure 2). The median Cu and Zn concentration on spider webs was about 10 times higher than in lichens. Such a situation was also observed when analyzing Ni and As content (accumulation ratio amounted to 84 and 22, respectively). In the case of Pb, the ratio was the lowest (about 3).

Taking into consideration the location of sampling points, most of the highest values were obtained in point number 8, which is consistent with the prevailing wind direction in this area (west wind), thus, it is probable that the concentration of metals there is elevated. The maximum value of Zn was estimated at point 8 (as well in lichens as on spider webs) reaching 185.17 µg/g and 1955.84 µg/g, respectively. The minimum level of Zn was noticed in point 10 for lichens (92.33 µg/g) and 7 for the spider webs (187.79 µg/g) (Figure 3). The presence of this metal in Legnica was analyzed by Konarski et al. [39]. In their study, the presence of Zn was noted in the closest vicinity of Legnica copper plant as well as in the city center (2 km NE of copper plants) and the concentration was two times higher when analyzing the particles from the copper plant. In our study, Zn was one of the three most frequently observed elements. Generally, Zn can be connected with particulate emissions from motor traffic [40] and it was proposed to be a tracer of vehicle emissions by Goix et al. [41]. Therefore, we also suppose that this factor has an impact in our case, as in the study area there are two big roads with heavy traffic nearby (roads: S3 and 3; Figure 1). Road 3 is a national road, while S3 is an express national road. According to the General Measurement Of Traffic, made in 2015, through road S3 cross about 15,000 motor vehicles daily and through road number 3 cross about 12, 000. What is more, in the study area, there is a provincial road located, with daily traffic around 9000 cars [42].

Studies by Konarski [39] showed that there was 340 times less copper in urban aerosol samples (2 km of copper plants) when comparing to the industrial dust. It indicates that high levels of copper in this area might be connected with the processes carried out by copper smelter "Legnica". In our research, it was also noticed that in the sampling points, located further away from KGHM, the lowest concentration of Cu was observed (points 3 and 4 for lichens; Figure 3). What is more, two of the highest results were recorded in the sampling points located west of the smelter (points 8 and 9 for lichens, reaching 371.67 and 206 µg/g, respectively). The maximum value of Cu in the spider webs was revealed in sampling point number 1 (4020 µg/g) (Figure 3). The differences between the accumulation in lichens and on spider webs were significant. The deposition of Cu on the spider webs varied between 166.45 and 4020 µg/g while accumulation in lichens ranged from 52 to 371.67 µg/g.

The maximum values of lead were estimated at 356.67 µg/g in sampling point 8 for lichens and at 1869.57 µg/g in sampling point 6 for spider webs (Figure 3). The lowest Pb accumulation in lichens was recorded in points 3 and 4 (the same points as for the lowest Cu content). This might indicate the possible air contamination by copper smelter "Legnica", whose main products are electrolytic copper and refined lead, only in the nearest parts, close to the smelter. The concentration of lead in lichens varied between 39.5 and 356.67 µg/g, while on spider web, the range was wider with 72.56 to 1869.57 µg/g.

Two of the highest levels of arsenic were found in points 6 and 8 for lichens (6.85 and 6.83 µg/g, respectively) and for spider webs (486.96 and 347 µg/g). The interesting thing is, that spider webs accumulated much bigger amounts of As (range from 33.29 to 486.96 µg/g) comparing to lichens, where accumulation was between 1.80 and 6.85 µg/g (Figure 3).

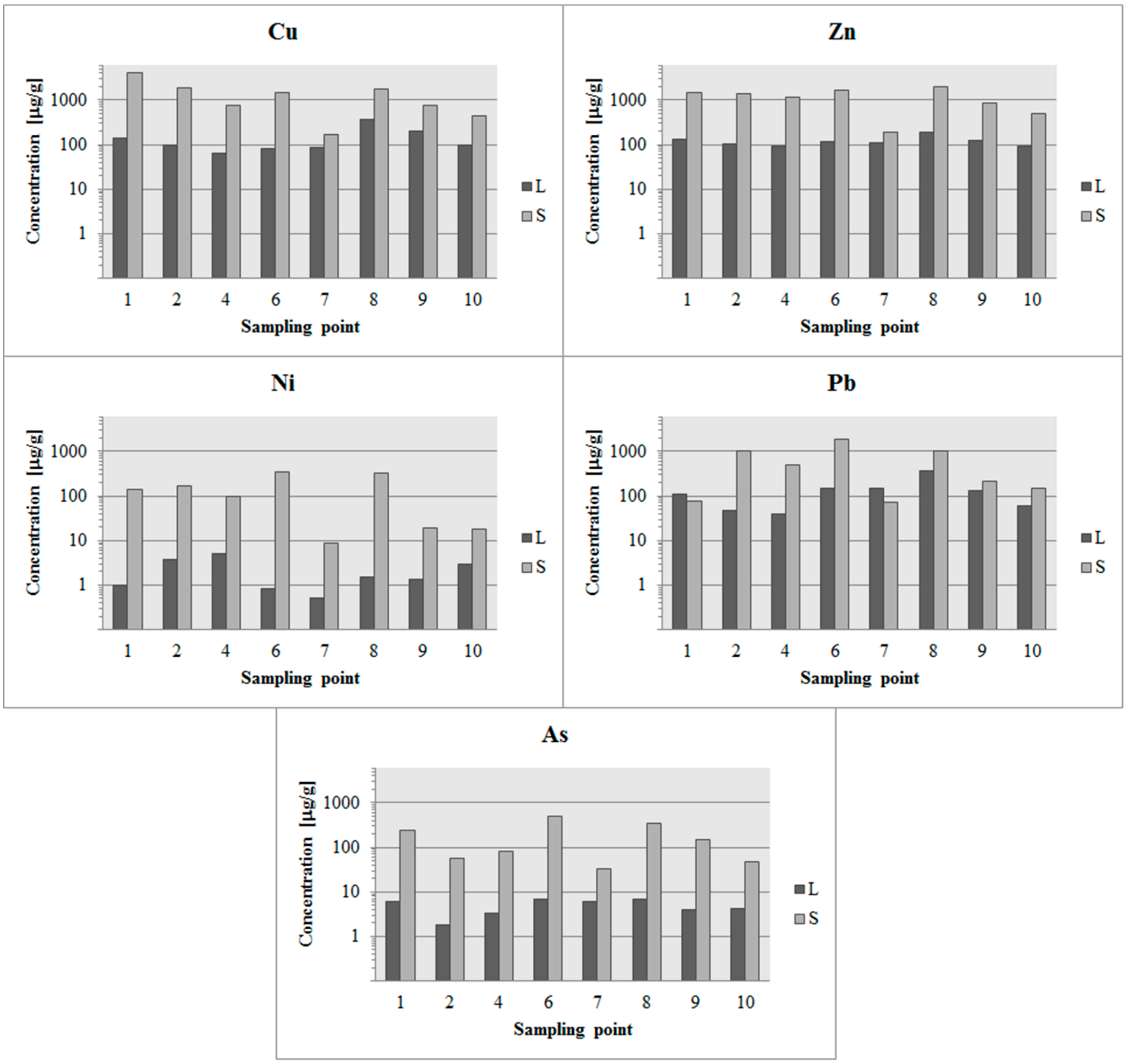

Figure 3. Comparison of each element concentration in lichens (L) and spider webs (S).

Additionally, quite large differences were observed between the ranges of accumulated nickel. Concentrations of Ni in lichens varied between 0.5 and 5 µg/g, and on spider webs between 8.54 and 347.83 µg/g. The maximum value of Ni for lichens was determined in point 4, which was inconsistent with the maximum level of Ni accumulated on the spider webs (sampling point 6). The minimal concentration for this element was found in point 7 in the case of both bioindicators (Figure 3).

Based on Figure 3, it can be easily noticed that the maximum values, when examining spider webs, were obtained in points 6 and 8 (both located far from residential buildings; point 6 situated close to mining part of the smelter, on the outskirts of the forest; point 8 positioned about 200 m west from the smelter in the middle of the forest). In the case of Cu, the maximum level for spider webs occurred in sampling point 1 (4020 µg/g). Despite the exact same exposition time, the concentration of analyzed elements in lichens was smaller in almost all cases, when comparing to metals content on spider webs. The exception was recorded only in points 1 and 7 for lead and concentrations in lichens were slightly higher.

3.1. Results of Contamination Factor (CF)

The calculation of CF in our study shows that in the case of Ni and Zn, the contamination is slight. More serious situations are observed for the level of Cu (severe contamination) or Pb which revealed extreme contamination (Table 2). This might confirm the main role of the smelter in the contribution of pollution in this region.

Table 2. Contamination factor results for lichens.

Metal	CF	Category
Pb	276.3	C6
Cu	25.7	C5
Ni	2.0	C3
Zn	2.2	C3
As	-	-

3.2. Results of the Shapiro–Wilk Test

The sets of metal concentrations in lichens and on spider webs were tested for normality using the Shapiro–Wilk test. The results are presented in Table 3. All the sets, except the set of Cu concentration in lichens, shows no significant difference from the normal distribution ($p < 0.01$).

Table 3. Results of the Shapiro–Wilk test for the concentration of elements in lichens and spider webs.

	Lichens					Spider Webs				
element	Cu	Zn	Ni	Pb	As	Cu	Zn	Ni	Pb	As
W-stat. value	0.75	0.82	0.87	0.79	0.91	0.85	0.96	0.87	0.84	0.86
p	0.008	0.05	0.17	0.03	0.37	0.11	0.87	0.16	0.08	0.12

3.3. Results of Tests Comparing Samples

Since only data about Cu concentration do not satisfy normality condition, the Wilcoxon test was used for Cu concentration and the Welch's t-test for other elements. The results of these tests are presented in Table 4. There is a clear difference between the concentration of Cu, Zn, Ni and As in lichens and on spider webs, while for the Pb, the equality of mean cannot be excluded. This is probably the result of similar ranges of concentration values obtained for both bioindicators as they varied from 39.5 to 1869.57 µg/g, although the values of Pb for lichens were significantly lower than those for spider webs.

Table 4. Results of the similarity tests between concentration in lichens and on spider webs at given site.

	Cu	Zn	Ni	Pb	As
Test	Wilcoxon	Welch's t-test	Welch's t-test	Welch's t-test	Welch's t-test
statistics	0.0	−4.8070	−2.9284	−2.1046	−3.0060
***p*-value**	<0.02	0.0019	0.0221	0.0715	0.0198
DOF	Not applicable	>7	>7	>7	>7

3.4. Results of Cosine Similarity

The sites were also checked whether the concentration in the lichens and concentration in the spider webs are similar or not, as the measure of similarity cosine similarity was used. The results are presented in Table 5. The obtained values show almost excellent agreement for sites 2, 4, 6, and 10, and very good agreement for sites 7, 8, 9. Only at point 1, metals content determined in lichens and on spider webs is not as similar as at sites mentioned previously, however, they are still with good agreement. This is mainly caused by Pb concentration.

Table 5. The values of cosine similarity between metal concentration in lichens and on spider webs.

	Point 1	Point 2	Point 4	Point 6	Point 7	Point 8	Point 9	Point 10
cos(θ)	0.81	0.98	1.00	0.98	0.85	0.89	0.90	0.97

Results of similarity analysis between lichens and spider webs at the given site 1, together with results of Welch's t-test, probably suggest that lichens and spider webs have similar sensitivity as bioindicators for Pb.

4. Discussion

The comparison of two completely different bioindicators, which are spider webs and lichens, have not been conducted before, thus, in the discussion, we are going to focus on comparing our results with other papers concerning either spider webs or lichens.

Analyzing the study conducted by Białońska and Dayan [43], where the lichen transplantation method was used (six months exposition), it can be noted that lichens are an effective tool in assessing the origin of pollution. In their work, the highest Zn and Pb levels were observed in the immediate vicinity of the Zn–Pb smelter "Bolesław" (mean 583 and 123.7 µg/g respectively). The zinc level in our research was almost five times smaller, while lead values were similar in both papers. Smelter "Bolesław" is a bigger smelter comparing to "Legnica", hence, in the research of Białońska and Dayan [43], Zn concentration was much bigger. The concentration of copper was one order of magnitude higher in the area of Legnica, which is not surprising, as in the studied area there is a copper smelter situated.

The database created by Koroleva and Revunkov [20] is said to be a "reference point" for monitoring studies. They collected wild lichens growing in the Kaliningrad region and Sambian peninsula and then analyses of trace elements concentration in the thalli of lichens were conducted. The exposition time of lichens on pollutants is unknown as the collection of in situ samples was conducted. In the case of Pb, Cu, Ni, Zn, the concentrations were higher in our studies. The differences were much bigger in the case of lead and copper. The content of As in lichens' thalli was not compared due to the fact that in the Koroleva and Revunkov study [20], this element was not analyzed. Based on their paper, contamination factor was calculated, using element levels noted in North Canada [25] as background. Analyzing our results, the highest CF was recorded for lead (C6), then in descending order, copper (C5), zinc (C3) and nickel (C3). Two out of four calculated contamination factors indicated a serious air pollution problem. Hence, it is supposed that this region is likely affected by anthropogenic emission. In comparison, the Kaliningrad region's contamination factor was estimated at the C2 category, with exception of two elements, and in the Sambian peninsula, most of the values were classified as C3 [20].

Comparing the accumulation of heavy metals on spider webs with literature results was a little bit more difficult. This is due to the limited number of studies. What is more, in each paper, different elements are considered, distinct spider webs are used and various exposition times are chosen.

Hose et al. [8] carried out analyses of zinc and lead, collected on webs of *Badumna socialis* and *Stiphidion facetum* in Australia. They noted 1400 and 800 µg/g for Pb and Zn, respectively, while in this research, it amounted to 613.2 µg/g for Pb and 999.1 µg/g for Zn. The concentration of lead, obtained by Hose et al. [8], was two-fold higher than recorded in this paper. When comparing zinc, the higher result was observed in Legnica, despite the fact that the exposition time in our case was three times shorter.

Xiao-li et al. [12] studied the webs of different spider species *Achaearanea tepidariorum* and *Araneus ventricosus*. The in situ webs were removed and after seven days, new webs were collected and analyzed for heavy metals contents (Pb, Zn, Cu, Cd). In the case of Pb, Zn and Cu, the levels in the area of Legnica were higher. It must be mentioned that in our study, the exposition time was much longer (two months). Additionally, in Legnica, where the copper smelter and refinery are located, explains why the values of Cu and Pb are one or two orders of magnitude greater in our work.

The comparison with analyses by Rybak [10], conducted in Wroclaw, Poland, seems the most appropriate as the exposition time was the same and collected webs were created by the same family of spiders. In all the cases, heavy metals content was higher in our study (for Ni: 139.7 μg/g and 24 μg/g, for Pb: 613.2 μg/g and 161.1 μg/g, for Zn: 999.1 μg/g and 553 μg/g, in Legnica and Wroclaw respectively). The biggest difference was noted for copper. The mean level of Cu amounted to 93.6 μg/g while its concentration in the present study was estimated at 1412.6 μg/g. Knowing the main pollutants in the area of Legnica, the difference is not that surprising.

Comparing the accumulation on spider webs and in lichens' thalli with papers mentioned above showed that the values obtained in the area of "Legnica" copper smelter are mostly higher than results presented by other authors. The elevated concentration levels may indicate a serious problem with the air quality in Legnica. This issue needs further investigation to examine if these concentrations of heavy metals can have a negative impact on humans' health and living organisms.

The interesting thing was observed when comparing these two bioindicators with each other. Lichens are known to be a good tool in assessing air quality and they are widely used. Our results show that the differences in elements' concentration in lichen thalli may depend on the localization of sampling point and distance from the smelter. Similar observations were noted when analyzing accumulation on spider webs. Additionally, the order of accumulated elements, arranged by quantities, was almost the same in both cases, which gives us a clear signal about the main pollutant in our study area. Even though the exposition time was the same, the significant differences were observed in the orders of magnitude of accumulated elements (Figure 3). The applied statistic tests suggest that lichens and spider webs have similar sensitivity as bioindicators for Pb only. This may lead to the conclusion that spider webs are a more effective bioindicator than lichens. In all the places where concentrations obtained by lichens analyses are low or below the detection limits, spider webs should be used to recheck the air quality. They can give interesting results even if the contamination in lichens is not observed. What is more, the sampling with spider webs could bring more advantages than applying lichens. Previous studies suggest that lichens had a greater affinity for atmophile elements (Hg, Cd, Pb, Cu, V, Zn) than mosses, and mosses' element composition was additionally influenced by soil, thus, it was necessary to do normalization of total element concentration to selected elements like As or Ti content to assess the origin of elements from the atmosphere [2]. The authors suggest that these two bioindicators cannot be used interchangeably as biomonitors and recommend epiphytic lichens for biomonitoring of atmospheric deposition of trace elements, except S compounds. On the other hand, the comparison between element concentrations in moss and lichen species (*Sphagnum capillifolium* and *Pseudevernia furfuracea*) proved that the moss is a more efficient metal accumulator and, unlike lichens, it is not affected by meteorological conditions such as drought [3]. In terms of these findings, the application of spider webs seems to be devoid of such drawbacks.

5. Conclusions

This research was supposed to compare the usefulness of two bioindicators: spider webs and lichens. The median accumulation in transplanted spider webs was far greater when comparing to lichens (in some cases, the differences were about one order of magnitude). Considering these two bioindicators' ability to accumulate selected elements, spider webs seem a better bio-passive sampler than lichens. Despite such great differences, the order of the most accumulated elements was similar in both cases, which indicates the possible source pollutant in this area. The concentrations of studied elements detected in lichens and spider webs after exposure in bags, and in Petri dishes in the vicinity of smelter, indicate that air is contaminated by trace elements such Cu, Zn, Pb, As and Ni.

The results of the similarity test showed a clear difference between the concentration of Cu, Zn, Ni and As in lichens and spider webs, with the exception of Pb, which suggest that sampling with the use of spider webs could be more efficient as they tend to accumulate higher concentrations of studied metals, thus they are probably more sensitive bioindicators than lichens. The revealed high concentrations of studied metals in both bioindicators confirm that the smelter plays a prominent role in air pollution in Legnica. Moreover, the presence of busy roads in the area may also contribute to emissions of metals.

The study confirms that spider webs are very efficient metal accumulators and could be used in the same way as lichens for bioindication of heavy metals contamination. Hence, we recommend using webs in all the situations when using lichens is improper due to for example lichens limited uptake of analyzed elements, by which the obtained results of accumulation would not be correct. The drought could also affect significantly the results obtained with lichens. Additionally, in the places where results received by analyzing lichens are below the detection limits, spider webs could be used to recheck the air quality. The usefulness of the spider web as a measuring device of mineral pollution in the other seasons of the year (e.g., winter) will be analyzed in further studies.

Supplementary Materials: The following are available online at http://www.mdpi.com/2071-1050/12/19/8066/s1, SM Table S1: Description of sampling points.

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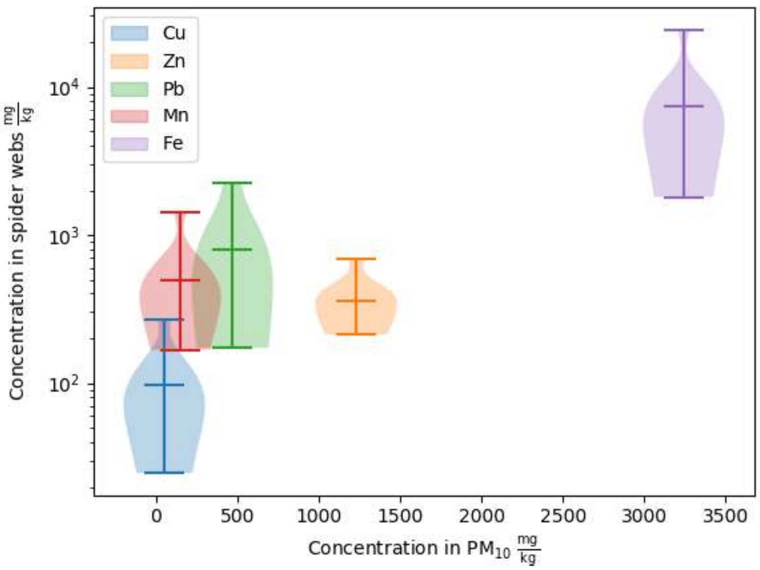
Artykuł 4

Porównanie kumulacji pierwiastków potencjalnie toksycznych przez sieci pajęcze z wynikami z aktywnego monitoringu powietrza (PM_{10})

Air pollution research based on spider web and parallel continuous particulate monitoring - a comparison study coupled with identification of sources. **Agnieszka Stojanowska,** Tomasz Mach, Tomasz Olszowski, Jan Stefan Bihałowicz, Maciej Górka, Justyna Rybak, Małgorzata Rajfur, Paweł Świsłowski. *Minerals*. 2021, vol. 11, nr 8, art. 812, s. 1-20.

W poniższej pracy wykonana została pierwsza próba testowania hipotezy, czy sieci pajęcze mogą dostarczać informację o zanieczyszczeniu powietrza zgodną z faktycznym stężeniem danego zanieczyszczenia, potwierdzonym przez referencyjne metody automatyczne. W tym celu wykorzystane zostały sieci pajęcze pająków z rodziny Agelenidae oraz analizator Horiba PX-375 służący do ciągłego automatycznego pomiaru stężenia cząstek stałych z wykorzystaniem analizy rentgenowskiej (XRF), który analizował w czasie rzeczywistym stężenie metali w cząstkach PM_{10}. Badania przeprowadzono w miejscowości Kotórz Mały w województwie opolskim. Wykorzystano sieci pajęcze znajdujące się *in situ*, a także sieci pochodzące z hodowli pająków w laboratorium. Czas ekspozycji bioindykatorów na zanieczyszczenia, jak i czas pracy analizatora automatycznego Horiba, wynosił jeden miesiąc. W próbkach sieci oznaczono: Fe, Pb, Zn, Cu, Mn, Cd, oraz Ni, a następnie wyniki porównano z wynikami uzyskanymi z analizatora Horiba PX-375. Otrzymane dane pozwoliły stwierdzić, że dla większości oznaczonych pierwiastków, z wyjątkiem Zn, stężenia na sieciach pajęczych były większe niż w przypadku wyników z analizatora Horiba (Rysunek 3). Wynikać to może z faktu, że analizator automatyczny pobierał tylko frakcję PM_{10}, stąd większe cząsteczki lub powstałe agregaty nie zostały przez ten sprzęt uwzględnione w końcowym stężeniu pierwiastków. W przypadku biomonitoringu z wykorzystaniem sieci pajęczych większe cząsteczki oraz agregaty nie zostały wykluczone, co spowodowało wzrost ilości zakumulowanych pierwiastków. Kolejnym wytłumaczeniem otrzymanych wyników może być też fakt, że bardzo drobne cząsteczki nie są w stanie zakumulować się na sieciach pajęczych z uwagi na specyficzne ułożenie nitek sieci, uniemożliwiających ich adsorpcję. Mimo zaobserwowanych różnic ilościowych, szereg stężeń pierwiastków, uporządkowanych malejąco, był dość podobny, szczególnie jeśli chodzi o pierwiastek występujący w najwyższych stężeniach (Fe) jak i w najniższych (Cu). Co więcej, wyniki procentowego udziału wybranych pierwiastków okazały się być bardzo podobne w obu testowanych metodach.



Rysunek 3 Stężenia pierwiastków na sieciach pajęczych w odniesieniu do stężenia mierzonego przez analizator Horiba PX-375 (Stojanowska et al., 2021).

W celu wytypowania źródeł zanieczyszczeń na badanym obszarze wykonano trajektorie wsteczne mas powietrza (model HYSPLIT). Zaobserwowano, że zanieczyszczenia transportowane są głównie z kierunków południowych, południowowschodnich i południowozachodnich, a ich źródło może być powiązane zarówno z polskimi ośrodkami przemysłowymi, zlokalizowanymi w pobliżu Kotórza Małego, jak i zanieczyszczeniami transgranicznymi transportowanymi z dalszych odległości.

Przeprowadzone badania wskazały na użyteczność sieci pajęczych w biomonitoringu powietrza, co już częściowo udowodniono we wcześniejszych pracach. Niniejsza praca podkreśla fakt, że pomimo widocznych różnic w ilości akumulowanych pierwiastków przez te dwa narzędzia (pasywne i aktywne) generalne trendy wynikowe są zbieżne. Biorąc pod uwagę różnice zaobserwowane przy analizie ilościowej zasugerowano, że w kolejnych tego typu badaniach należałoby dokonać porównania z frakcją $PM_{2,5}$, a także pyłem całkowitym (TSP).

Wniosek: Istnieją różnice w ilościowej akumulacji zanieczyszczeń przez sieci pajęcze i analizator zbierający frakcję PM_{10}, natomiast trendy wynikowe są zbieżne.

minerals

Article

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

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.

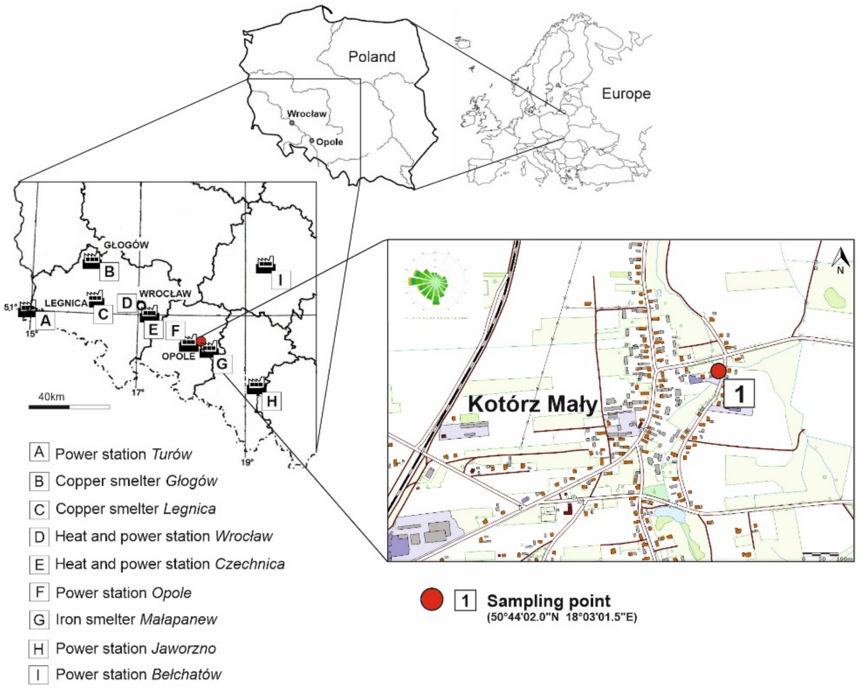

Figure 1. Location of the study area.

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]:

$$EF = \frac{\frac{C_{x,m}}{C_{Al,m}}}{\frac{C_x}{C_{Al}}} \tag{1}$$

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 $\frac{\text{ng}}{\text{m}^3}$, 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.

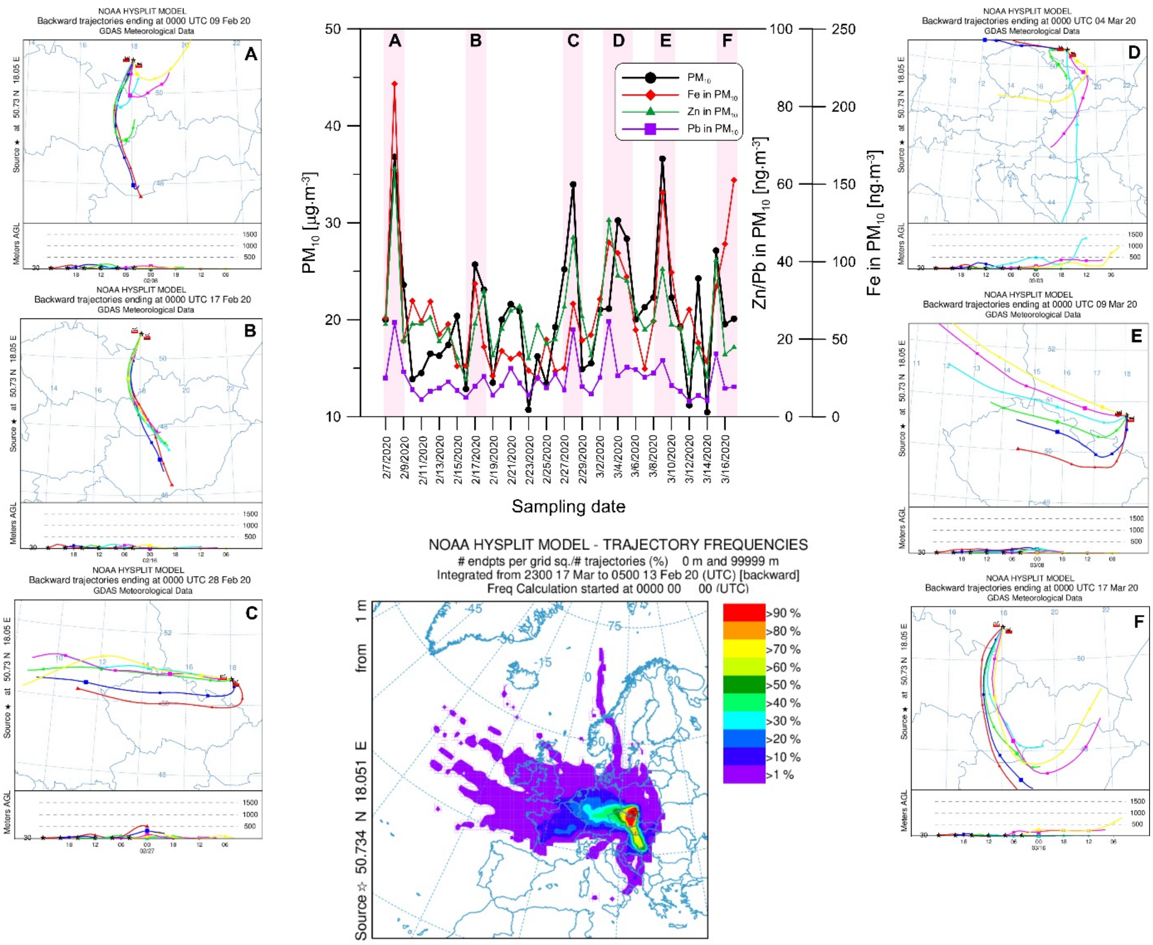

Figure 2. HYSPLIT trajectory frequencies and 24 h air backward trajectories in Kotórz calculated for given episodes (**A**–**F**).

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·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).

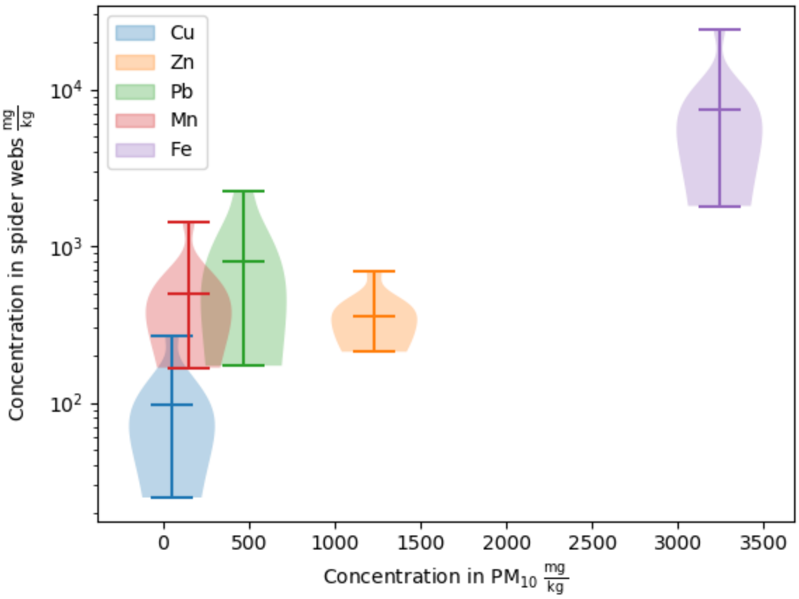

Figure 3. Concentrations in spider webs with relation to the concentration measured by Horiba PX-375. The horizontal position of the violin is the total concentration of PM_{10} while in the vertical direction the violin represents the distribution of concentration.

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.

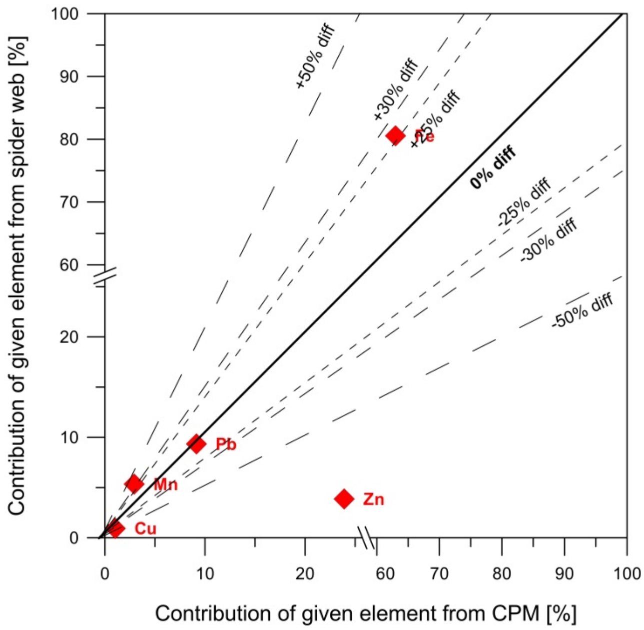

Figure 4. The comparison of both applied methods (spider web and CPM) for assessing the air pollution (% of difference).

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.

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Artykuł 5

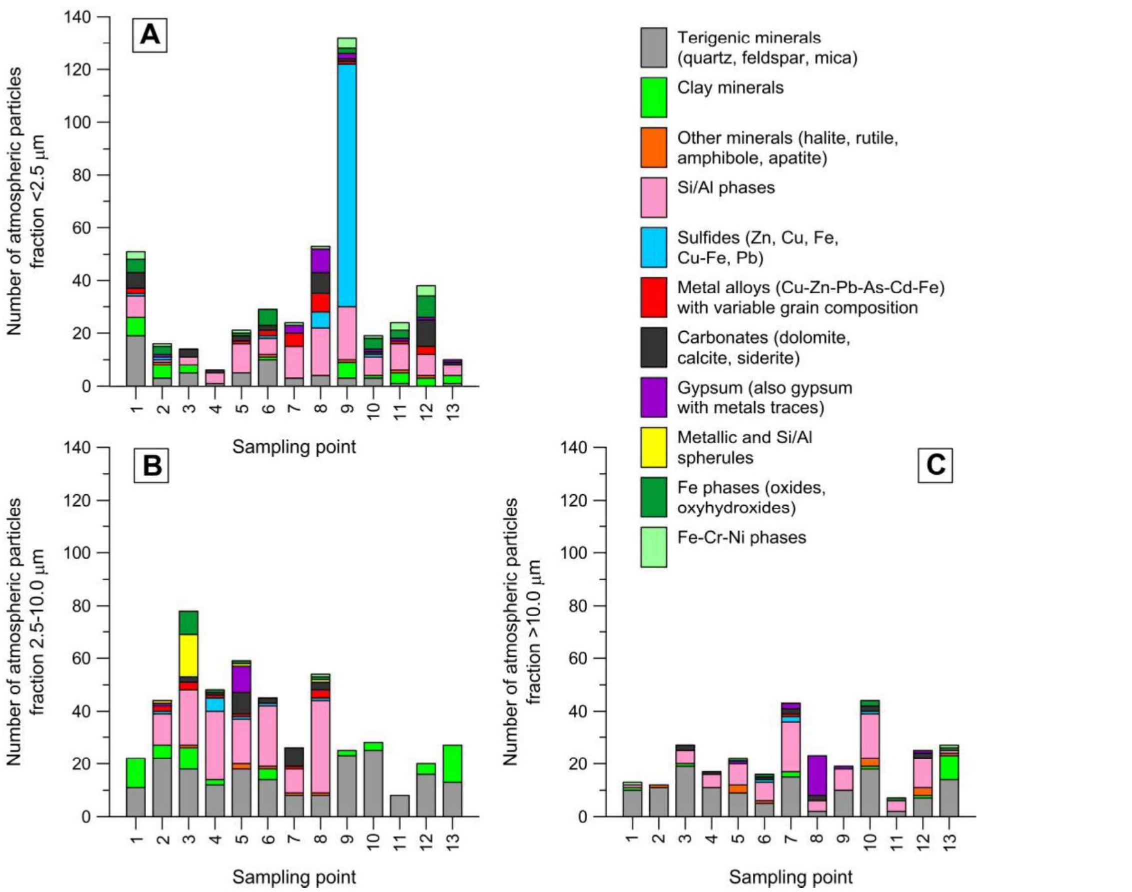
Porównanie wyników otrzymanych z analizy cząsteczek zakumulowanych na sieciach pajęczych z wykorzystaniem SEM-EDX z wynikami otrzymanymi z ICP-MS - charakterystyka zanieczyszczeń

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. Wojciech Bartz, Maciej Górka, Wojciech Bartz, Justyna Rybak, Radosław Rutkowski, **Agnieszka Stojanowska.** *Chemosphere*. 2021, vol. 278, art. 130454, s. 1-14.

W tej pracy przedstawiono szczegółową analizę pierwiastkową i mineralogiczną cząsteczek zdeponowanych na sieciach pajęczych. Celem pracy, było nie tylko ilościowe i jakościowe scharakteryzowanie zakumulowanych zanieczyszczeń, lecz także porównanie wyników, otrzymanych z dwóch wybranych metod: skaningowej mikroskopii elektronowej z systemem spektrometrii rentgenowskiej (SEM-EDX) oraz spektrometrii mas sprzężonej z plazmą wzbudzaną indukcyjnie (ICP-MS). Próbki sieci pajęczych (pająków z rodziny Agelenidae i Linyphiidae) eksponowane były na zanieczyszczenia powietrza w Głogowie przez okres trzech miesięcy. Dzięki analizom wykonanym z wykorzystaniem SEM uzyskane zostały informacje dotyczące kształtu, formy i wielkości cząsteczek, a także ich potencjalnego pochodzenia. Wykonane analizy składu pierwiastkowego z wykorzystaniem ICP-MS pozwoliły na uzyskanie konkretnej informacji na temat ilości zakumulowanych wybranych pierwiastków (Zn, Pb, Cd, Cu, Ni, As). Analiza otrzymanych wyników pozwoliła na stwierdzenie, że cząsteczki zakumulowane na sieciach pajęczych w różnych punktach poboru były mocno zróżnicowane pod względem wielkości i chemizmu (Rysunek 4). Grubsze frakcje występowały w mniejszych ilościach i charakteryzowały się mniejszym zróżnicowaniem pod kątem mineralogicznych (głównie cząsteczki naturalne). Dla odmiany, drobniejsze frakcje pojawiały się w większych ilościach i były bardziej zróżnicowane (głównie cząsteczki antropogeniczne). Dodatkowo, analiza statystyczna potwierdziła, że pierwiastki potencjalnie toksyczne skorelowane były silniej z drobniejszą frakcją, niż z frakcją grubszą. Finalnie porównana została częstość występowania konkretnych pierwiastków, zaobserwowanych przy analizie z wykorzystaniem SEM z frekwencją pojawiania się tych pierwiastków przy analizie ICP-MS. Stwierdzono, że wyniki uzyskiwane z obydwu metod mogą być porównywalne. Dodatkowo, dzięki mapom przestrzennego rozmieszczenia cząsteczek różnych frakcji uwzględniających cząstki antropogeniczne i naturalne, udało się określić realny zasięg danych frakcji zanieczyszczeń.

Reasumując, można stwierdzić, iż sieci pajęcze po raz kolejny dowiodły swojej użyteczności przy ocenie jakości powietrza, a analiza porównawcza dwóch metod analitycznych wskazała, że w niektórych przypadkach wykorzystanie SEM do rozpoznawania zanieczyszczeń może z powodzeniem zastępować wykorzystanie droższej metody ICP-MS.

Wniosek: Cząsteczki zakumulowane na sieciach pajęczych zdominowane były przez drobniejszą frakcję, a ich charakterystyka mineralogiczna wykazała, że były to głównie cząsteczki pochodzenia antropogenicznego. Wyniki analizy zakumulowanych cząsteczek z wykorzystaniem SEM-EDX i ICP-MS są porównywalne.



Rysunek 4 Zróżnicowanie cząstek zakumulowanych przez sieci pajęcze w 2018 r. w okolicach huty miedzi w Głogowie (Bartz et al., 2021).

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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

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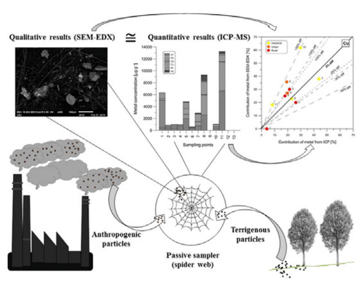
HIGHLIGHTS

- Particulate matter is easily adsorbed on spider webs.
- SEM analysis can be considered a cheaper and more detailed method than ICP.
- Percentage contribution of metals identified by SEM is comparable with ICP results.
- Correlation between mineralogical and geochemical analyses of PM was revealed.

GRAPHICAL ABSTRACT



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ABSTRACT

Air pollution can be monitored using many different methods. In this paper, we aimed to test and validate two analytical techniques based on complex mineralogical and geochemical analyses with the use of spider webs as a passive sampler. The samples of spider webs were collected in 2018 in polluted areas in the vicinity of the copper smelter Głogów (Poland). Samples were analysed using scanning electron microscopy with energy dispersive x-ray analysis (SEM-EDX) to obtain not only the information about the form and size of studied particles but also their origin (anthropogenic or terrigenous). Geochemical analysis was performed using inductively coupled plasma mass spectrometry (ICP-MS), providing the total amount of chosen and potentially toxic elements. The frequency of metal occurrence in atmospheric particles identified with the use of SEM-EDX was compared with the results from ICP-MS and recalculated into the percentage of contribution. A significant correlation between chemical and mineralogical composition was found demonstrating that the phases and minerals were correctly recognised and properly divided into groups. For elements such as Pb, Zn, and Cu, which are the major contaminants in the study area, the validation of the method gave good results, revealing the convergence of results for most sampling points. Finally, our study showed that the results obtained by SEM-EDX analysis can be comparable to quantitative results (ICP-MS analysis).

1. Introduction

Particulate matter (PM), also known as atmospheric aerosol

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particles, is a mixture of solid and liquid particles that are suspended in the air. Its chemical composition, morphology, and size varies, depending on time and location. Therefore, two different sources of PM origin can be distinguished, natural and anthropogenic. Mineral dust, wildfires, sea salt, volcanic eruptions, and biological particles are considered natural sources of PM. In turn, anthropogenic sources originate mainly from industrial processes, fuel combustion, or transport (Klimont et al., 2017). Among atmospheric total suspended particles (TSP), we can distinguish different groups depending on particle size. Hence, PM is divided into: coarse particles (PM_{10}) with a diameter 2.5 μm < d ≤ 10 μm, fine ($PM_{2.5}$; 0.1 μm < d ≤ 2.5 μm), and ultrafine particles ($PM_{0.1}$; d ≤ 0.1 μm) (World Health Organisation, 2000). The smallest particles are the most dangerous, as they can enter deep into the lungs and, in some cases, they can be permanently trapped there (Hsu et al., 2016). Special attention should be given to ultrafine particles, which are known to be very hazardous because they can be absorbed into the bloodstream and eventually accumulate in organs (Oberdörster et al., 2004; Takenaka et al., 2001), while the coarse fraction of TSP is likely to affect the laryngeal and nasal area (Martonen et al., 2002). Currently, PM, especially of an urban origin, is of great concern, as it affects human health and, at high concentrations, causes respiratory diseases that often lead to premature deaths (World Health Organisation, 2013). According to the European Environment Agency's report, in 2014, fine particulate matter led to almost 400,000 premature deaths of European Union citizens, especially children (EEA, 2017; Ghosh et al., 2018; Guo et al., 2018; Jena et al., 2019). People living close to industrial areas are at higher risk and often struggle with respiratory diseases (Bergstra et al., 2018). To counteract this issue, the European Union obligates all Member States to monitor air quality with the use of active methods (e.g., gravimetric or optic), which gives very precise results. Unfortunately, the use of reference methods (active methods) is not always possible due to the demand for specific equipment that is relatively expensive. Among these inconvenient situations, biomonitors are a good solution, as they are inexpensive, easily accessible, and simple to use. Biomonitors are widely applied in assessing air quality in urban and industrialised areas, and among them, the most popular are lichens (e.g., Massimi et al., 2019; Parviaine et al., 2019; Vannini et al., 2019), mosses (e.g., Kosior et al., 2015a,b; Schintu, 2005), leaves or needles of trees (e.g., Górka et al., 2020; Teper, 2009), or tree bark (e.g., Chrabąszcz and Mróz, 2017). The application of spider webs when assessing air quality is a relatively new idea. There have been several studies demonstrating that this tool can be a good passive sampler for particulate matter; therefore, its use is becoming increasingly popular (Górka et al., 2018; Hose et al., 2002; Rutkowski et al., 2019; Rybak, 2015; Rybak et al., 2019a,b; Xiao-li et al., 2006). One of the first papers on this topic showed that the accumulation of elements on spider webs was dependent on the age and distance of the source (Xiao-li et al., 2006), indicating their usefulness as indicators of potentially toxic elements (PTE). Based on those findings, other studies (e.g., Rybak, 2015; Rybak et al., 2019a) focused on the evaluation of the usefulness of spider webs in biomonitoring pollution and came to similar conclusions, recommending the use of this tool for the assessment of PTE concentrations and Polycyclic Aromatic Hydrocarbons (PAHs). Recently, research has made a step forward and in the paper of Górka et al. (2018), the SEM-EDX technique was used for the first time for the identification of various inorganic particles adsorbed on spider webs, which caused interest in the subject and the desire to explore it. One of the most important advantages of applying spider webs is that they commonly occur; spiders are present in both the natural and polluted environment, and their webs are easily accessible. Furthermore, the method is cheap, non-invasive, and organic, as it does not produce extra products that need to be degraded. The additional advantage is that spiders weave their webs in secured places; therefore, they are prevented from destruction by heavy rain or strong wind. The particles of air pollution deposit on the web and, depending on whether they contain heavy metals, accumulate in the web, while some organic compounds can be bound by chemical affiliation, e.g., PAHs can be built into the protein matrix of spider webs.

To contribute to the development of this method we applied spider webs in a heavily polluted area in the vicinity of the copper smelter Głogów (proGEO, 2018; The City Council in Głogów- City Development Department, 2019) to conduct a complex mineralogical and geochemical analyses on the basis of spider webs. The smelter reduced the emission of harmful substances in the 1990's (Strzelec and Niedźwiecka, 2012), although the studied area still struggles with exceeding the established limits for air pollution (Environment Protection Program for the City of Głogów (proGEO, 2018)). Additionally, according to the Report on the state of the Głogów City Commune for 2018 (The City Council in Głogów- City Development Department, 2019), the level for arsenic in PM10 in Głogów is systematically exceeded (in 2013, it was 16.0 ng/m^3, in 2014–14.5 ng/m^3, in 2015–12.2 ng/m^3, in 2016–12.6 ng/m^3, and in 2017–30.2 ng/m^3, while the target level for arsenic in PM10 dust is 6 ng/m^3). Thus, both analyses (mineralogical and geochemical) were conducted to identify the pollution accumulated on spider webs. Usually the mineral particles of the dust originate from anthropogenic activity, i.e., mining, gas, coal, or metallurgical industries, or they are linked to the Earth's crust (in the form of oxides, carbonates silicates, and aluminosilicates) (Boev et al., 2013). To determine the specific sources of the pollution, studies using SEM-EDX were conducted in terms of chemical, morphological, and mineralogical analyses, which are crucial for defining the pollution origin. We applied SEM-EDX analyses to assess the mineralogical composition of collected dust, and scaled SEM photography was used to determine the size distribution. Simultaneously, inductively coupled plasma mass spectrometry (ICP-MS) analyses were performed to assess the concentrations of selected elements (Zn, Pb, Cd, Cu, Ni, As) that are likely to contaminate the study area.

The aim of this research was to evaluate the statistical significance between chemical and mineralogical composition of spider webs exposed to pollutants in the vicinity of a smelter, therefore, determining if the results obtained by SEM-EDX analyses are comparable to quantitative results (ICP-MS analyses) and vice-versa. Unlike ICP-MS, SEM-EDX analyses are cheaper and more accessible. Additionally, ICP-MS results only provide the total amount of elements, while SEM-EDX gives information about the form and size of the studied particles. The division by size is particularly important as different fractions can be hazardous for humans to varying degrees. The usage of these two methods in biomonitoring have already been presented by (Catinon et al., 2009), but the passive sampler used for PM collection was different. In our paper, however, the novelty is in the comparison of results from SEM with ICP with the use of spider webs, which has never been done before. In a previous paper by Górka et al. (2018), it was presented that air pollution deposited on spider webs can be successfully analysed with the use of SEM, however, it is unknown if the use of SEM is comparable with very precise ICP analysis.

Considering that spider webs have already been shown to be a good passive sampler for air pollution monitoring (e.g., Rybak et al., 2019a; van Laaten et al., 2020; Xiao-li et al., 2006), we hypothesised that: 1) analyses of particulates deposited on webs is sufficient to assess the impact of the smelter; 2) it is possible to distinguish natural and anthropogenic particles; and 3) consideration of different sizes of particles will allow us to estimate the range of the smelter impact. To summarise, this paper does not focus only on a typical description of the impact of smelter on the environment based on assessing PTEs in the study area with the use of biomonitors. We aimed to test and validate both methods (ICP-MS and SEM-EDX) with the use of spider webs. Such an approach has never been applied before for spider webs, which are only now being used to monitor the environment, and we believe that the results of our study provides a new direction in the future application of spider webs for such studies.

2. Materials and methods

2.1. Study area

Głogów is a city located in the southwestern part of Poland (Lower Silesia voivodship), where the biggest European centre of copper mining and processing is situated. According to the data provided by the company, **K**ombinat **G**órniczo-**H**utniczy **M**iedzi KGHM (Copper Mining and Metallurgical Combine) is the sixth source of electrolytic copper and the first largest silver producer in the world. KGHM also produces gold, palladium, platinum concentrate, lead, and rare earth elements in smaller quantities. Additionally, the company also extracts rock salt (https://kghm.com/). The climate on Lower Silesia is relatively humid and belongs to a temperate continental climate. In proximity of the city, there are also heat and power stations located in Wrocław, Czechnica and a power station in Turów (Fig. 1).

The Głogów copper smelter was established in 1971 and was known to emit high amounts of SO_2, NO_2, PM, and PTEs. After the restrictions imposed by Ministry of the Environment, Natural Resources and Forestry in January 1990, the smelter was obligated to limit its negative impact on the environment, which led to a significant reduction of harmful substances (Strzelec and Niedźwiecka, 2012); however, there is still a problem with pollution in this area. Kostecki et al. (2015) reported that copper and lead levels in the litter horizon and topsoil near Głogów exceeded the limits for these elements in industrial areas (Kostecki et al., 2015). The impact of transport contributes significantly to pollution in this region. The area of Głogów is crossed by national road number 12 and several provincial roads, 292, 319, and 329. According to the General Measurement of Traffic (Generalny Pomiar Ruchu) (GDDKiA, 2015) by road number 12, 19,000 motor vehicles pass through this area per day (measured at roundabout Konstytucji 3-maja). Additionally, the provincial roads are known for heavy traffic, varying from 3860 (road 292) to 15,000 cars daily (road 329; GDDKiA, 2015).

2.2. Spider species characteristics

In this study, webs of two different species belonging to family Agelenidae and Linyphiidae were used. Both families weave large, dense webs, which helps to attract particulate matter. We chose two common species *Eratigena atrica* C.L. KOCH, 1843 (Agelenidae) and *Linyphia triangularis* (Clerck, 1757) (Linyphiidae) that have been used previously and have proven their utility in the accumulation of particles (e.g., Rachwał et al., 2018). The selection of families used for studies is also dependent on the species occurring in the study area. Agelenidae weave a tubular funnel-shaped web with a retreat at the end of a sheet, which is made from dry, not sticky but dense silk (Roberts, 1995). Agelenids are nocturnal, and they can be encountered in darker areas, such as flower beds, wood piles, and around houses, especially abandoned, neglected buildings and bridges, tunnels, and car parks. Females of *Eratigena atrica* are active all-year-round, but males are active only from July to October. This species is particularly common in abandoned places but also in forests (Roberts, 1995). Linyphiidae are known as sheet web spiders because the majority of family representatives weave sheet-like webs and the spider hangs under the web, with threads above and below the web, which allow it to catch prey (Roberts, 1995).

A few studies (Hose et al., 2002; Rybak et al., 2019b) demonstrated that PTEs found on spider silk are not embedded inside the matrix of webs, suggesting that the deposition of PM is only due to the mechanical suspension of dust particles in the deep network of web meshes. This is especially true for non-sticky webs (Agelenidae and Linyphiidae), as these types of webs are dense, and particulate matter can be deposited easily among web meshes.

2.3. Methods

2.3.1. Sampling collection

Spider web samples were collected from mid-June to mid-September in 2018. Thirteen sites were chosen within the area of Głogów (sampling points 1–13; Fig. 1; SM Table 1). Old webs from all sampling points were removed and only new construction was

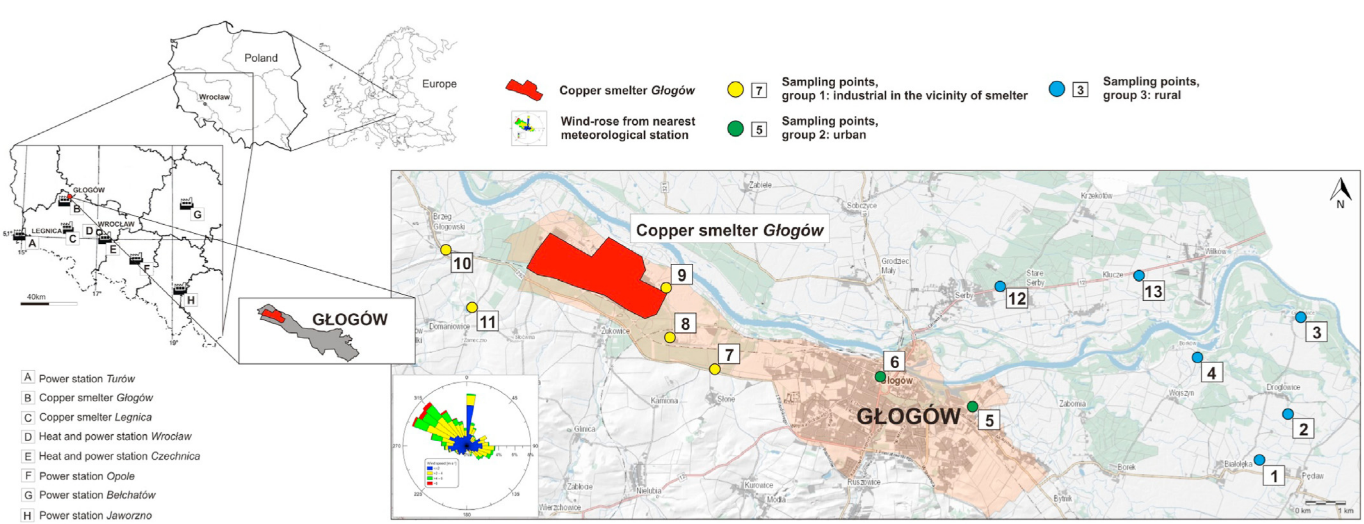

Fig. 1. Location of sampling points (spider webs from Agelenidae and Linyphiidae family): (No 1-13) in Głogów vicinity.

taken for further studies. The exposure time was 3 months and we assume that the PM was deposited on webs from the 1st day of exposure to the end of the experiment. In our studies, we obtained the average mixture of PM from the above-defined period deriving from any random day within 3 months of webs' exposure. To obtain the new web, sampling points were visited daily, and the activity of spiders was observed. The new webs were noted and collected after a defined exposure time. For the collection of webs, we used glass Petri dishes that were sterilised before they were used in the sampling area. Then, the Petri dishes with webs were covered directly after sampling, secured with adhesive tape, and transported to the laboratory. The webs, suspended on the frame of each Petri dish, were then stored pending further investigation.

Additionally, for further analyses, the sampling points were divided into three groups according to their characteristics: group 1—industrial in the vicinity of smelter (sites 7, 8, 9, 10, 11); group 2—urban (sites 5 and 6); and group 3—rural (sites 1, 2, 3, 4, 12, 13). The division was made to check if there were significant differences between specific locations and to analyse the range of smelter-like particles.

2.3.2. SEM-EDX analyses

The chemical composition of PM deposited on spider webs from Głogów was determined with the use of a scanning electron microscope equipped with an energy dispersive x-ray analyser (SEM-EDX). Samples were carefully transferred with the help of two tweezers to a glass-slide, avoiding folding of the spiders web which would give us unreliable measurements. The glass was previously covered with double-sided sticky carbon strips, coated with carbon (to achieve approx. 30 nm) using the Cressington 108C Auto Carbon Coater equipped with MTM-10 High Resolution Thickness Monitor. Then, prepared samples were analysed 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). The SEM was operated at 14 kV acceleration voltage and at high-vacuum mode. The whole surface of each sample was scanned at a low magnification to reveal possible heterogeneity in the spatial distribution of deposited particulate matter. Subsequently, spots within the representative areas were randomly chosen, and a set of microphotographs were taken for each sample, with a magnification of 100 × , 500x, 1000 × , and 2000 × . The total analysed area was c.a. 1 mm^2 per specimen. EDX microanalysis was performed with 120 s of capture time, 50 to 100 counts per second, and 20% dead time, recording the EDX analysis at the central part of the particles. The minimum detection limit of EDX analysis was 0.2 wt%. To distinguish terrigenous particles from anthropogenic phases, we compared the obtained EDX spectra with the data presented by Reed (2005) and Deer et al. (2013). In all cases, when the chemical analyses of the particles differed from the chemical composition of minerals, the particles were considered anthropogenic. Additionally, before classification into anthropogenic and natural particles, the geological structure of the surface formations of the analysed area were studied. On this basis, mineral phases that did not occur on the surface of the study area were also classified as anthropogenic (e.g., sulphide phases, which do not occur in natural formations on the surface). Similar methodology was also presented in Górka et al. (2020). Obtained SEM images were studied with the use of JMicroVision software (Roduit, 2007). The Feret max (the longest Feret diameter) for each PM was found and used to determine the size distribution of collected particles. The determination of the size of analysed particles led to the division of mineralogical phases into size-dependent groups. Eventually, the obtained data was used to prepare charts of the mineralogical phases in different fractions (Grapher™ from Golden Software, LLC, Golden, CO, USA, www.goldensoftware.com) and to construct the maps of spatial distribution of anthropogenic atmospheric particles, considering the fractions (Surfer® from Golden Software, LLC, Golden, CO, USA, www.goldensoftware.com).

2.3.3. ICP-MS analyses

Inductively coupled plasma mass spectrometry (ICP-MS) analyses were performed using an Elan 6100 DRC-e Perkin (Perkin Elmer, Waltham, MA, USA), and the concentration of six elements (Zn, Pb, Cd, Cu, Ni, As) was determined in spider web samples. These analyses were performed to determine the exact quantity of considered pollution and to identify the pollution source. Firstly, webs samples were weighed (approximately 0.06 g) and then were flooded with 3 mL of nitric acid (Suparpur, Sigma-Aldrich) and heated at 80–90 °C for 6 h. The resulting mixture was filtered through a 0.22-μm PSE membrane filter and analysed with ICP-MS. The following operating conditions were established: ICP RF 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. The samples were analysed in triplicate. For calibration solutions, we applied certified multi-element standard stock solutions of Periodic table mix 1 and Transition metal mix 2 (Fluka). We used two certified reference materials, SRM 1643e [recovery in the range 95(Ni)–116%(Cr)] and SRM 1648a [recovery in the range 75(As)-127%(Cr)] to validate this method. They were obtained from the National Institute of Standard and Technology (NIST). The solid CRM 1643e and 1648a were digested in the same way as spider web samples. The analysis was done by the central laboratory of Institute of Environmental Engineering Polish Academy of Sciences in Zabrze. The Institute's Laboratory works in accordance with the PN-EN ISO/IEC 17025 norm. The following detection limits were established: 0.151 μg/l for Zn; 0.018 μg/l for Cd, 0.134 μg/l for Pb, 0.019 μg/l for As; 0.017 μg/l for Ni; and 0.048 μg/l for Cu.

2.3.4. Statistical analyses

The normality of the analysed features was checked using the Shapiro–Wilk's W test. Spearman's correlation coefficients were calculated (Sokal and Rohlf, 2012) to examine the ρ of the relationship between the contribution percentage of anthropogenic origin, atmospheric particles adsorbed on spider webs represented the three different size groups, related metal concentrations, and emitter locations. Differences among the sampling sites (rural, industrial, and urban) in contribution of atmospheric particles adsorbed on spider webs were assessed by one-way analysis of variance (ANOVA). Homogeneity of variances was checked with a Levene test. We applied post-hoc a HSD Tukey test to check the contribution of anthropogenic atmospheric particles adsorbed on spider webs among the three groups of sites (Sokal and Rohlf, 2012). The calculations were done with Statistica 13.1 software (Dell Inc., 2016).

2.4. Meteorological/environmental parameters

In general, in 2018, the annual average temperature in most of the voivodship amounted to 10 °C, which was high when compared to previous years. This year was also very dry, and the sum of precipitation was not higher than 80% of the average annual precipitation observed in 1971–2000 (Żyniewicz et al., 2019). The prevailing winds blew throughout the Lower Silesia voivodeship from west to east (Dancewicz et al., 2009).

In 2018, in the area of the Lower Silesian voivodeship, the levels of sulphur dioxide, as well as carbon monoxide, were not exceeded. In the case of NO_2 the admissible level of the annual average was exceeded only in the measuring station in Wrocław, while the rest of the voivodship was normal. The concentrations of Pb, Cd, and Ni in PM_{10}, were not higher than the average in the studied area, while the average annual level of As in PM_{10} was above acceptable levels, amounting to 10.04 ng/m^3. In the rest of the voivodeship, the concentration ranged from 1.44 to 4.57 ng/m^3 (Żyniewicz et al., 2019). These measurements were recorded on Wita Stwosza Street in Głogów.

The regional scale observations were constructed based on Hysplit back trajectory models for Głogów (Rolph et al., 2017; Stein et al., 2015). The 24 h back trajectories were calculated for each day for 15.06–15.09.2018 period and finally prepared in ArcGis 10.7.1 Software (SM Fig. 1B) as one multiple trajectory model.

3. Results and discussion

Analyses of sampling points showed the differentiation of particles accumulated on spider webs (Fig. 2). In site 4 (Fig. 2A), K-feldspar and quartz were recorded, which are minerals originating

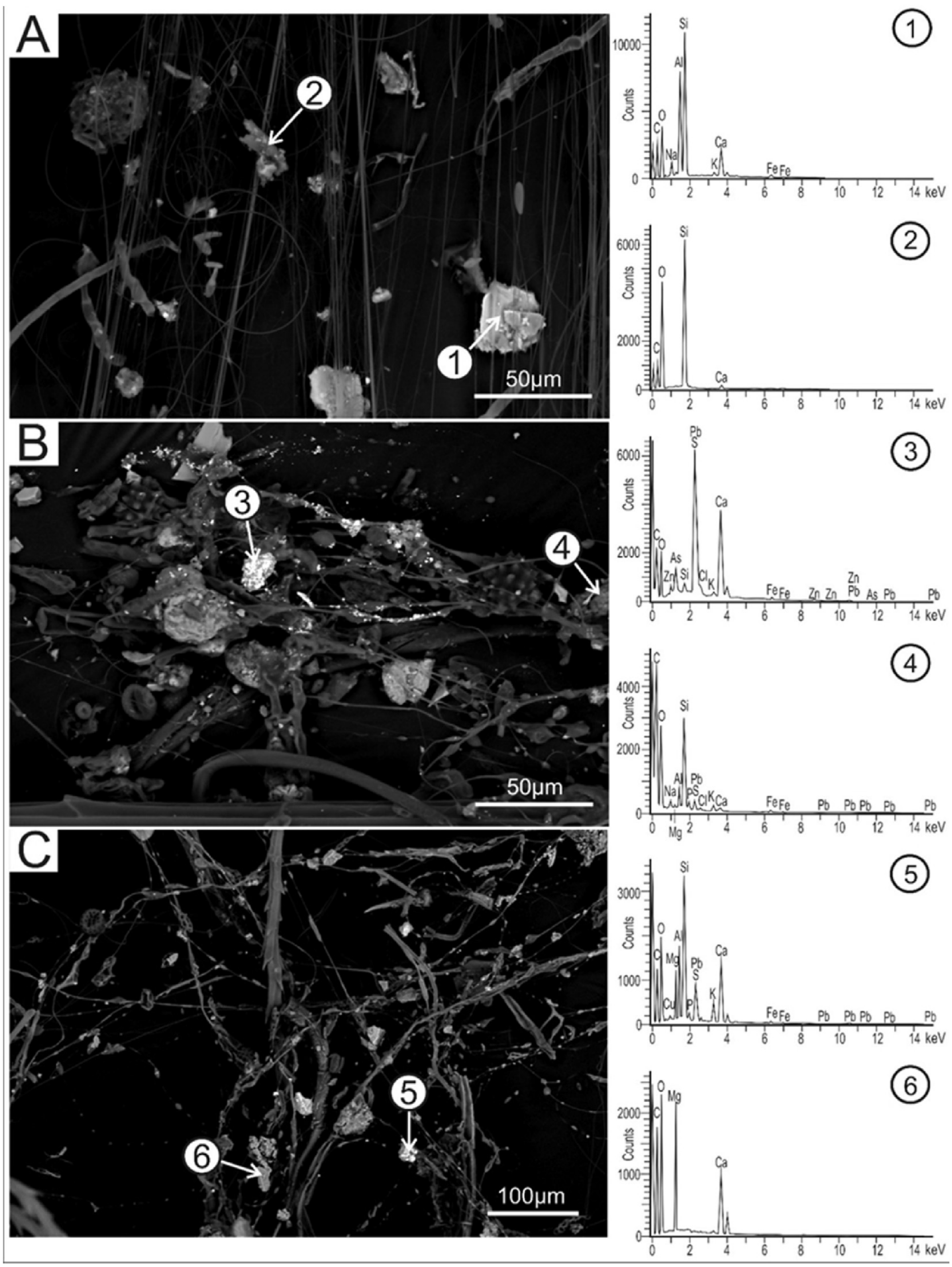

Fig. 2. BSE images of spider web taken from Głogów smelter site 4 (A), 9 (B) and 7 (C) and representative EDX spectra. Spectrum 1 – K-feldspar, spectrum 2 – quartz, spectrum 3 – galena + sphalerite + calcite, spectrum 4 – silicate glass with Pb, spectrum 5 – silicate glass with Pb/Cu sulphides, spectrum 6 – dolomite.

from the Earth's crust (e.g., soil deflated) (Anake et al., 2016; Byeon et al., 2015). In contrast, sampling points 7 and 9 (Fig. 2C and B, respectively), presented particles related to the pollution produced by the smelter, as there were many particles with Pb and Cu. Additionally, the location of these points was more favourable to enhance the accumulation of particles of smelter origin because both sites were situated in the close vicinity of smelter industry objects. The comparison of BSE images suggested that the particles from natural sources (e.g., Earth crust) were of a larger size, while particles of anthropogenic origin were usually found in the smaller fractions.

Applying SEM-EDX for analyses of the composition of PM adsorbed on spider webs was done by Górka et al. (2018), who confirmed this as a reliable technique to identify various particles. Górka et al. (2018) analysed the particles collected on webs in the city of Wrocław and demonstrated that particles originating from the activity of the smelter in Głogów were not present, which excluded the occurrence of impacts of long range transport (80–90 km) from this smelter in Wrocław. Most of the analysed inorganic particles were found to be connected with soil deflation and building weathering. The recent investigation in the Głogów vicinity confirmed that natural particles derived from the Earth's crust were also present in significant amounts, predominating in the larger fractions. Within the groups of smaller sizes, many particulates originating from the activity of the smelter were found.

3.1. Mineralogical composition

3.1.1. Mineralogical phases and PM fraction

Considering the diversification of PM, we distinguished 11 groups of analysed particles (Fig. 3). Three of the first groups were considered terrigenous, originating from soil deflation. The rest of the mineralogical phases were connected with the anthropogenic activity of the direct smelter industry, as well as industry connected with smelters, such as desulphurisation systems and flotation enrichments. The discrimination between terrigenous and anthropogenic particles was carried out based on the idea from Pachauri et al. (2013) and Górka et al. (2020), and the modification to local industry characteristics were considered.

The contribution percentage of phases were calculated for each point and fraction by dividing the amount of the given phase (mineral particles) by the amount of total particles and multiplying the result by 100. Then the percentage contribution of inorganic anthropogenic origin particles (IAP) was determined. The calculations were held according to the following equation:

$$\%contribution\ of\ IAP = (100\% - (\%\,Q + \%\,OT))$$

where Q stands for quartz and OT stands for other terrigenous minerals [i.e., alkaline feldspar, biotite, chlorite, clay minerals (e.g., illite and kaolinite), garnet, plagioclase, muscovite, rutile, zircon].

The group with the largest particles was represented mainly by terrigenous minerals and anthropogenic Si/Al phases. High amounts of silica phases in the area of the Głogów copper smelter

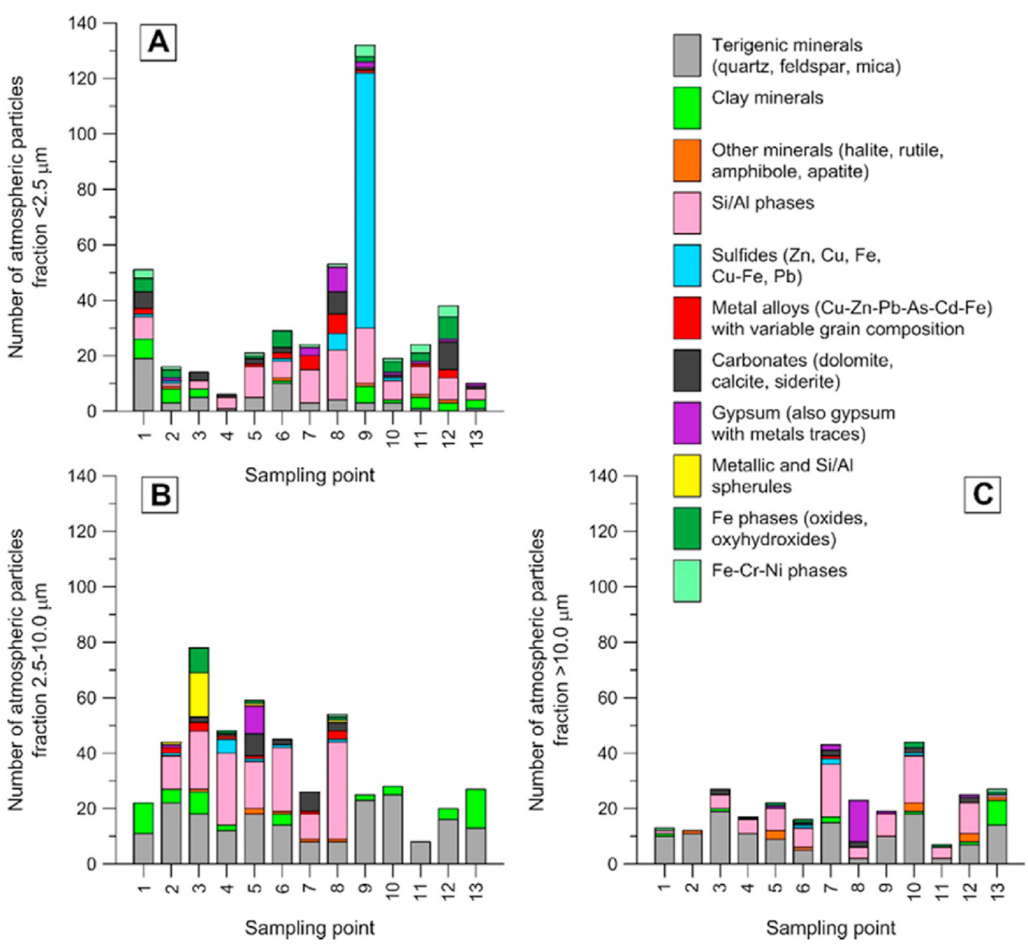

Fig. 3. Summarized SEM-EDX results. Mineralogical phases reported for particles deposited on spider webs collected in 2018 in Głogów smelter vicinity.

originated from the mobilisation of fine silica grains by convector gases (SO_2, N_2, O_2), which are produced during copper smelting (Muszer, 2004). The smallest fraction ($PM_{2.5}$) was the most diverse and showed a small input of terrigenous groups and a larger contribution of anthropogenic ones, indicating the impact of the smelter (e.g., metal bearing particles, like Fe phases, sulphides, and Fe–Cr–Ni phases). This was consistent with the fact that natural PM, such as windblown dust, is characterised by a larger hydraulic diameter when compared to anthropogenic PM, which tends to have smaller sizes (Chtioui et al., 2019). Additionally, in the paper of Hueglin et al. (2005), elements emitted by anthropogenic processes were found in the smallest analysed fraction (PM2.5). The Si and Al phases (i.e., in the form of spherules or amorphic phases) were found in significant amounts in all fractions (almost in all the sampling points), indicating the impact of anthropogenic activity. The presence of S-rich particles in the smallest fractions is usually assigned to be an indication of anthropogenic impact (Matassoni et al., 2011). The data presented in this article revealed noticeable amounts of sulphides, mainly in finer fractions that could be taken as a marker of the influence of anthropopressure. Due to its presence in the inhalable fraction, the health of nearby residents is under severe threat. In addition, the metals alloys were mostly recorded in the smallest fraction, which indicates industrial combustion processes (Armon and Hänninen, 2015; Laden et al., 2000; Zanobetti et al., 2009). In contrast, a large part of the coarse fraction was represented by earth crust components (e.g., silicates, aluminosilicates, and carbonates) (Brunekreef and Forsberg, 2005).

The mineralogical composition of deposited particles varied with sample site, but terrigenous minerals were consistently present. Moreover, some particles of clay minerals were recorded, which is consistent with the fact that sandy loams and loamy sands predominate in this area (Kostecki et al., 2015). Sampling point 9, located closest to the smelter (east of the smelter) was characterised by the highest content of sulphides and the highest number of atmospheric particles of the fraction < 2.5. At another sampling point, also located close to the smelter (8), a noticeable amount of sulphides and metal alloys were observed. Additionally, an interesting situation were observed at point 3, far from the smelter in the rural area (in the fraction 2.5–10), where some metallic and Si/Al spherules were observed, while in the other locations, this amount was negligible. An unexpected occurrence of smelter-like particles were noticed in point 3 (rural area). This point was located close to a small road, and the observed particles could be connected with the proximity to a minor sub-road. To produce the bituminous asphalt mix material, of which some minor roads are made in Poland, rock aggregates are used, as well as artificial aggregates (e.g., blast furnace slag) and recycled aggregates (according to Adamczyk et al., 2012). Therefore, we presumed that the abrasion of road material led to the occurrence of smelter-like particles at this rural point.

3.2. Spatial distribution of anthropogenic particles

Before spatial analysis of the obtained data, we tested a hypothesis concerning the significant influence of (i) local scale meteorological conditions (predominant wind direction and wind speed), as well as (ii) regional scale (air mass transported for long way) meteorological conditions, on dispersing atmospheric anthropogenic pollutants derived from the Głogów smelter.

Wind rose for the period of sampling (15.06–15.09.2018) from Legnica, which is the nearest possible weather station, located about 66 km south from Głogów (SM Fig. 1A), indicating that for local dispersion, we observed the prevailing wind from the WNW/NW. Therefore, we expected the largest impact in the eastern region. The pollutants easily settled not in the closest vicinity of smelter but travelled further and settled in Głogów (urban area), which exceeded the arsenic concentration in the air in the city of Głogów (The City Council in Głogów- City Development Department, 2019).

Similarly to data obtained for local (near surface) air mass directions (SM Fig. 1A), higher (500 m. a.g.l) regional air masses were transported mainly from the W/WNW direction. Therefore, we expected that metal bearing atmospheric pollutants would be transported E and ESE from the Głogów smelter. Moreover, a lack of important influence on air masses from the south excluded, in our opinion, the influence of second metal bearing atmospheric emitters in this region, i.e., Legnica smelter (Fig. 1), in the general pool of analysed particles identified on spider webs.

According to Klein (1993) and Teper (2009), particulate matter containing metal particles can be easily transported, reaching even the areas located far from the source; therefore, the maps of the spatial distribution of anthropogenic atmospheric particles were presented (Fig. 4).

The smallest particles, marked as anthropogenically originated, were easily transported with the wind stream (Fig. 4A), while the behaviour of larger particles was strongly influenced by gravity and the friction layer. PM emitted at a low height cannot travel with the wind stream for a long time and settles on the ground quickly (Phalen and Phalen, 2013). Therefore, the coarse anthropogenic fraction was likely to be found in the closest area of the emitter, while the range of smaller fractions was wider (Fig. 4B and C). Additionally, the direction the particles moved was consistent with the dominating wind direction in this area (Dancewicz et al., 2009). Fig. 4A, representing the distribution of $PM_{2.5}$, shows smaller concentrations of anthropogenic $PM_{2.5}$ just above the city of Głogów, while the concentration around the city was higher. This situation might be connected with two different processes: (i) urban heat island phenomenon, in which, due to human activities, the urban area is significantly warmer than the surrounding areas (Masumoto, 2015). When the inflowing air mass from the west and southwest reaches the city (warmer area), the spin movement of particles occurs and particles flow around the city. The second reason could be (ii) intensified traffic in the city coupled with higher urban processes, which generate large amounts of terrigenous particles, reducing the fraction of small anthropogenic particles.

Considering the above situation, KGHM's impact could negatively influence the neighbouring towns. In the research conducted by Muszer (2004), the impact of the considered smelter (Głogów) was also observed in the neighbouring areas, located 5 and 10 km south from the metallurgical complex, even though the dominant wind was different. In contrast, Samecka-Cymerman et al. (2009) showed that, based on analyses of moss and soil samples, the contamination by Cu in Legnica, reached the surrounding areas, up to 15 km in all directions (except north). Considering both examples and the wind direction (SM Fig. 1A), we can claim that the impact of the Głogów smelter can be seen especially on the leeward side, but we are aware of the fact that other parts can be affected as well. Based on Fig. 4, the estimated range of analysed fractions $PM_{2.5}$, $PM_{2.5\text{-}10}$, and PM_{10} was about 10, 6, and 3 km, respectively.

3.3. Analysis of metals identified on spider webs

Pollution, produced by Cu-smelters, mainly originated from smelting and refinery processes and occurs in the form of particles, bearing toxic elements, such as As or Pb (González-Castanedo et al., 2014). In our study, metals identified on spider webs varied with sampling points in terms of quantity and quality (Fig. 5). Zn and Pb

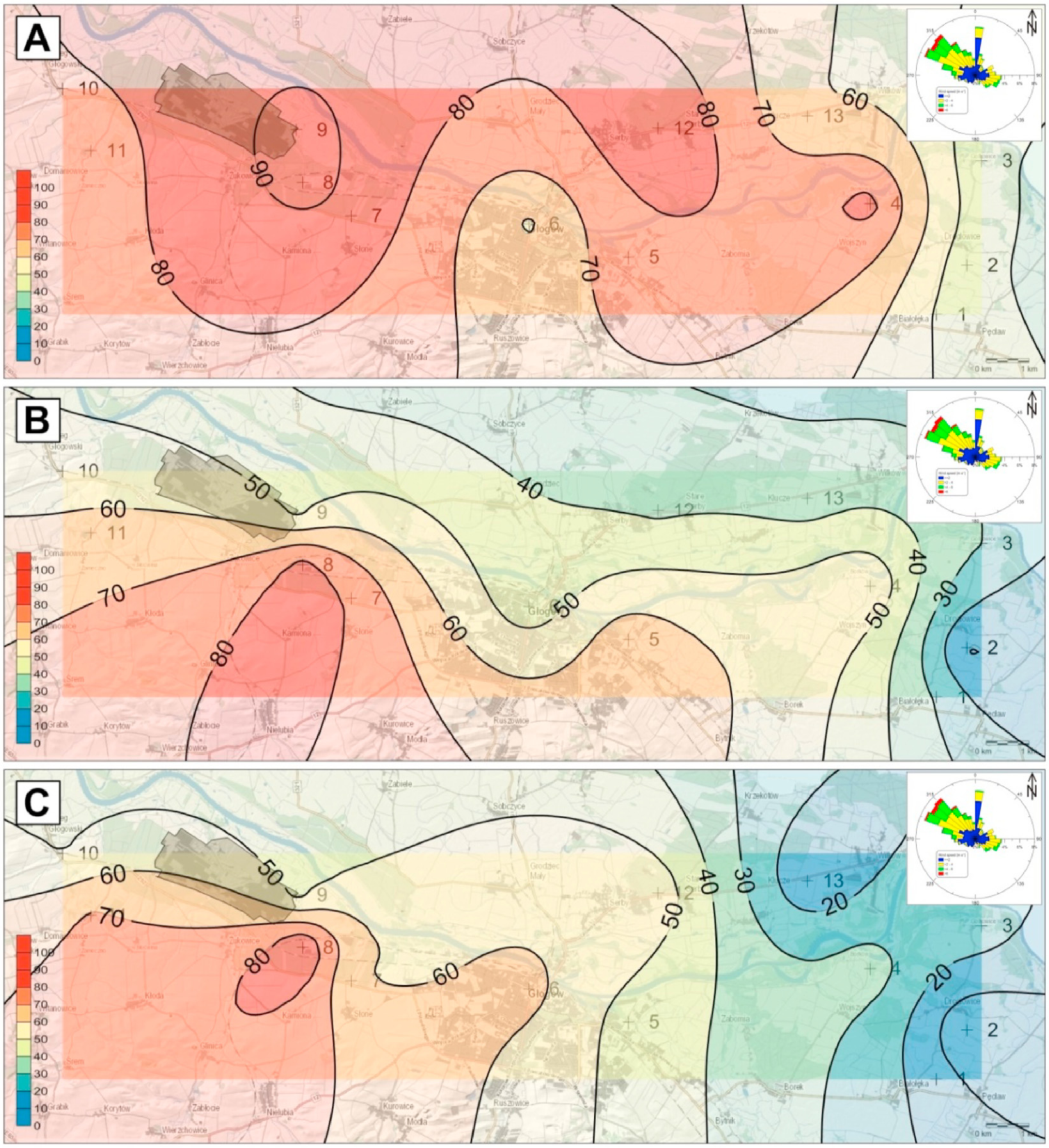

Fig. 4. Spatial distribution of anthropogenic atmospheric particles (see the method of separation in the text) fraction PM2.5 (A), PM2.5-10 (B) and PM10 (C) deposited on spider webs in Głogów smelter vicinity.

were the most abundant, while Ni and As occurred occasionally. However, knowing the strong toxicity of As, this issue is still of big importance. According to the World Health Organisation (WHO), the emission sources of As, such as smelters, cause an elevated risk of lung cancer in nearby populations (WHO, 2019). Particles of Cu were observed in all sampling points, but Cd was only noted in sampling point 1. Spider webs located the furthest away from the smelter (sites 1–4) trapped similar amounts of metals (no more than 2000 μg/g), with the exception of point 1, where a high content of Cd inflated the results. The highest level of metals occurred in point 11 (almost 14,000 μg/g), which was located close to the smelter but was not on the leeward side.

The characteristics of atmospheric aerosols from Głogów, carried out by Muszer (2007) in 2004–2005, were consistent with our results. Muszer (2007) reported the presence of Cu, Pb, Ni, and Zn sulphides and metallurgical alloys with a diverse composition (Cu–Zn, Pb, Pb–Cu) (Muszer, 2007). Moreover, analyses of the soil samples in the vicinity of copper smelting confirm contamination mainly by anthropogenic Pb but also Zn and Cu (Samecka-Cymerman et al., 2009; Tyszka et al., 2016). Spider webs from Wrocław (Poland), analysed by Rybak in 2015, revealed much lower values of Pb, amounting to 161 μg/g, while, in our study, the Pb concentration reached up to a few thousands of μg/g. Additionally, the values for Cu noted by us were higher than in Wrocław. In some points the concentration of Zn were similar in both studies (about 500 μg/g); however, a few sampling points in our study stood out, revealing a Zn concentration an order of magnitude higher [sampling points 5 (urban site), 8, and 11 (industrial sites in the vicinity of the smelter)].

3.4. Comparison and validation of applied methods (ICP-MS and SEM-EDX)

It was crucial to check the possible relationship between the chemical (metal concentrations) and mineralogical composition of atmospheric particles. To analyse the relationship between

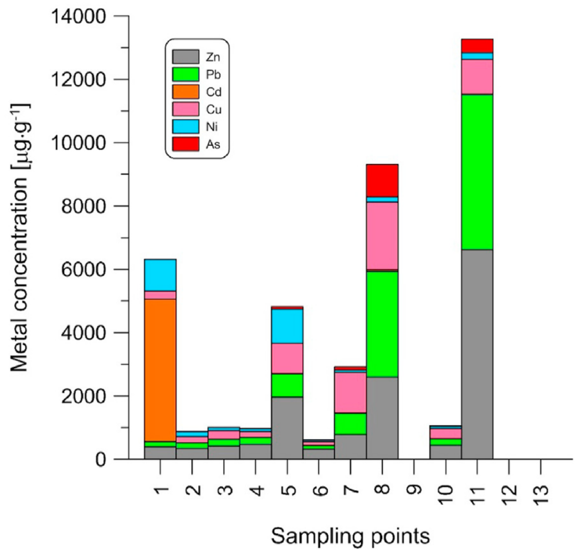

Fig. 5. Summarized ICP-MS results. Metal concentrations of spider webs gathered during 15.06–15.09.2018 in vicinity of Głogów smelter (SW Poland).

different elements, the correlation coefficients (ρ) were calculated (Table 1). A very strong correlation was observed between Zn and Pb. In addition, the data showed strong agreement between Cu and other elements (except Ni), which were consistent with the results obtained by Muszer (2007) and revealed that the spherules of Cu–Ni were the least abundant when analysing the spherules from slag from Głogów (Muszer, 2007). Thus, we presumed that Ni was not very abundant in the dust, and the weakest correlation with other metals was observed for Ni. In contrast, Cd revealed a moderate correlation with all metals (0.42–0.59), but the value for Cd–Cu was higher (0.65) (Table 1).

In the case of almost all elements, strong agreement was noted with anthropogenic $PM_{2.5-10}$, which is a respirable fraction (Gurjar et al., 2010). Particles of Zn were found in the groups of small fractions ($PM_{2.5}$ and $PM_{2.5-10}$), while Pb and Cu mostly in $PM_{2.5-10}$. Interestingly, As revealed a strong correlation with $PM_{2.5}$, $PM_{2.5-10}$, and PM_{10}, indicating that it can be dispersed in all fractions. According to a Wojewódzki **I**nspektorat **O**chrony **Ś**rodowiska WIOŚ (Province Inspectorate Of Environmental Protection) report, the origin of As is usually connected with point emission (industrial factories) (WIOŚ, 2017). Additionally, Dimitrijević et al. (2009) demonstrated that a large portion of anthropogenic As originates from Cu production. Therefore, it can be concluded that here the apparent impact of smelter on environment is observed.

The statistical analysis also showed that there was no correlation between Ni and different fractions, nor between Ni and other metals; thus, we presumed that Ni was not present in the form of minerals but only as admixtures, and therefore its origin cannot be solely associated with the activity of the smelter. The possible source of Ni could be attributed to local road traffic and the wear of automotive brake pads containing small amounts of this element (Kukutschová et al., 2011). There was also no correlation between Cu and different fractions, but a strong correlation between Cd and Cu was found. Therefore, the connection of Cd to the activity of the smelter could not be excluded.

To summarise, PTEs were found mainly in the finer anthropogenic fractions ($PM_{2.5}$ and $PM_{2.5-10}$), causing a serious threat to the environment and human health. Considering the possibility of the smallest particles to travel deep into the lungs or enter the blood system, reaching all organs, and knowing the toxicity of heavy metals, such a distribution of metallic particles is a serious health hazard. The particles determined in this study contained the following elements: Zn, Pb, Cu, As, Ba, Ag, Ni, and Cr. The majority of these elements, such as Pb, Zn, Cu, Cr, and As, have a strong negative impact on human health. We calculated the percentage share of these elements in the total sum of particles, as determined with the SEM-EDX (Fig. 6) in studied sites. In general, the largest contribution percentage was noted for Cu and Zn, reaching maximally 38% (sampling point 7) and 40% (sampling point 3) of studied particles, respectively. Mean values can, however, provide a better view of the situation. In this study, almost one-fourth of particles contained Cu, while one-fifth contained Zn. Additionally, the occurrence of Pb was often notable, with the highest input reaching 35.7% (sampling point 6) and an average of 17.5%. The rest of the elements were less frequent and were identified in 10% or less of particles. Despite the small average input of As in all particles and the fact that it was not observed in each sampling point, its occurrence should not be treated with less importance. In some sampling points (8 and 9), As reached more than 20% of all particles, and in others, like 5, 6, and 12, it accounted for about 15%. Considering the given numbers and the fact that As was commonly present in all size fractions, its strong negative impact on human health cannot be overlooked. In the case of sampling point distribution, for sites situated in the vicinity of the smelter and within Głogów city (sites 5, 6, 7, 8, 9, 10, and 11), elements related with the activity of the smelter, such as Cu, Zn, and As, predominated. Other elements, such as Ni, were found mainly in rural areas, suggesting other source of contamination. Nevertheless, no elements should be neglected when considering their impact on the inhabitants of Głogów and neighbouring areas. Therefore, certain steps must be undertaken to avoid the spread of contamination and protect the health of local populations.

Table 1
Spearman's correlation coefficients ρ between the data analysed for Głogów sampling points. The significant correlations ($p < 0.05$) are marked by bold font.

	Zn [μg/g	Pb [μg/g]	Cd [μg/g]	Cu [μg/g]	Ni [μg/g]	As [μg/g]	Distance from emitter [m]	Direction from emitter [°]	Anthropogenic $PM_{2.5}$	Anthropogenic $PM_{2.5-10}$	Anthropogenic PM_{10}
Pb [μg/g]	**0.98**										
Cd [μg/g]	0.55	0.42									
Cu [μg/g]	**0.82**	**0.79**	**0.65**								
Ni [μg/g]	0.43	0.43	0.59	0.35							
As [μg/g]	**0.95**	**0.90**	0.59	**0.89**	0.25						
Distance from emitter [m]	**−0.64**	−0.55	−0.38	**−0.68**	0.14	**−0.79**					
Direction from emitter [°]	0.47	0.35	0.47	0.58	−0.13	0.61	−0.85				
Anthropogenic $PM_{2.5}$	**0.64**	0.55	0.28	0.55	−0.14	**0.75**	−0.82	0.54			
Anthropogenic $PM_{2.5-10}$	**0.84**	**0.81**	0.33	**0.76**	0.09	**0.92**	−0.83	0.53	0.70		
Anthropogenic PM_{10}	0.59	0.54	0.25	0.55	−0.18	**0.73**	−0.90	0.76	0.59	0.74	
Total metals [μg/g]	**0.78**	**0.70**	**0.92**	**0.79**	**0.67**	**0.77**	−0.50	0.49	0.35	0.54	0.50

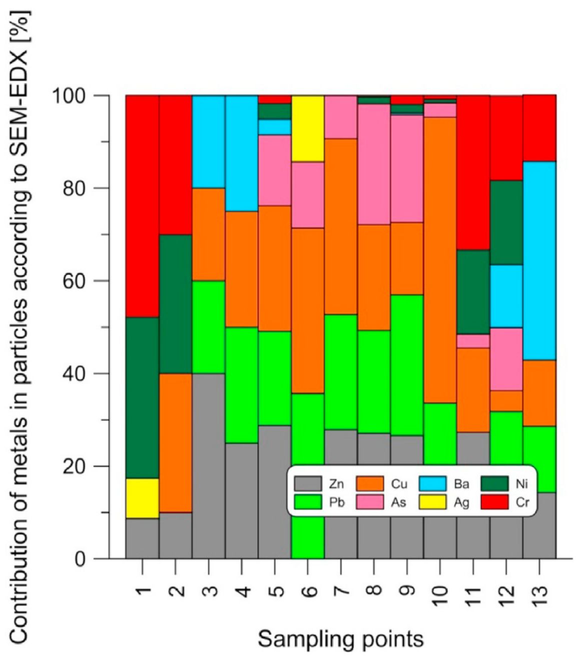

Fig. 6. Frequency of occurrence of individual metals in atmospheric particles determined with SEM-EDX [%].

The dependence between different fractions of particles and the distance from the emitter showed a strong negative correlation (Table 1), indicating the connection of analysed particles with emissions from the smelter. Furthermore, a strong negative correlation was observed for Zn, Cu, and As and the distance from the smelter, highlighting the input of the smelter on the emission of these elements to the atmosphere.

Additionally, we conducted one-way ANOVA to detect differences among these three groups: 1—industry/smelter, 2—urban, and 3—rural for their contribution of different particle sizes adsorbed on spider webs. The test revealed that groups differed significantly ($P < 0.05$) (SM Table 2). The post-hoc HSD test confirmed a statistically significant relationship ($P < 0.05$) between groups 1 (smelter) and 3 (rural) for particles 2.5–10 μm and for particles > 10 μm, but not between groups 1 (smelter) and 2 (urban) and groups 2 (urban) and 3 (rural) ($P > 0.05$). For particles <2.5 μm, all types of sites (groups 1–3) did not differ significantly, indicating that the smallest particles could spread everywhere. Larger particles (2.5–10 μm and >10 μm) settled in the urban sites (within Głogów city) and did not travel further to the rural areas as there were significant differences between these two types of sites (group 1 smelter and group 3 rural). These results are in agreement with previous studies on the spatial distribution of particles (e.g., Górka et al., 2020), demonstrating further dispersion of smaller particles. The similarity between smelter sampling points and urban sampling points found here was not surprising and reports presented by the Main Inspectorate of Environmental Protection (2020) confirmed that in the urban area, where their measurement station is located, there is an exceeding arsenic concentration in the dust, regardless of the season of the year, which is another point of smelter impact.

Finally, we compared the frequency of occurrence of individual metals in atmospheric particles using SEM-EDX (Fig. 6) with the results from ICP-MS (Fig. 5) converted into a contribution percentage. The comparison of ICP-MS and SEM-EDX analyses in the terms of Zn content showed that the application of both methods were comparable for some of the sampling points, especially for those with the biggest impact of pollution from the smelter (industrial sites: 7 and 8, located on the leeward side; Fig. 7). Additionally, the identification of this metal by SEM-EDX analysis at points 1 and 3 was very precise. Conversely, for sampling points 5 (urban), 11 (industrial), and 4 (rural), the differences ranged from 25 to 50% (underestimation). Large differences for Zn were recorded between the two methods for industrial site 10, which was probably connected with the dominant wind direction (SM Fig. 1) and windward location of this site (the amount of this element was four times lower on spider webs assessed by SEM-EDX than ICP-MS). A similar situation was found for rural site 2, which probably resulted from the distance between this point and the smelter. For urban site 6 (city centre of Głogów), the ICP-MS method revealed the lowest total content of metal (Fig. 5). Therefore, even if the contribution of Zn in the total metals was about 50% (Fig. 7), its amount was very low. The precise interpretation of metals with SEM-EDX was difficult due to the small amount of particles found on the spider web. The situation can be connected with the urban heat island phenomenon (Fig. 4). Additionally, it cannot be excluded that most of the particles of Zn in this sample were present in the smallest fraction (<$PM_{2.5}$), which would hinder its correct identification by SEM.

Analyses of Pb in spider webs showed almost complete agreement between both methods for urban sites 5 and 6, rural sites 3 and 4, and industrial sites 7 and 10. Moreover, the results for industrial site 8 and urban site 6 did not exceed 50%. The biggest differences were recorded for rural sites 1 and 2, located far from the smelter, and industrial site 11, situated on the windward side. The concentration of Pb in the ICP-MS method for both rural sites was very low (Fig. 5); therefore, in SEM-EDX, it was easy to overlook this element (Fig. 6). Moreover, the lack of Pb on spider webs collected from industrial site 11 was probably connected with the dominant wind direction (SM Fig. 1) and windward location of this site. In the points where SEM-EDX lacked certain elements, even though ICP-MS showed that they were present, the studied metals could occur in the form of very small particles (dispersed metals) so that their analyses with SEM-EDX was impossible.

The case of Cu showed the most satisfying results. The differences between both methods were not bigger than 30% (Fig. 7). The metal content in industrial site 8 was found to be the best estimated, as no differences were recorded between the methods. Additionally, proper identification was done for point 7. Notably, both sites were situated on the leeward side, presenting pollution strictly connected with the smelter. For other sites (urban sites: 5, 6, industrial sites: 10, 11, and rural sites: 2, 3, 4) differences did not exceed 50% (mostly about 25–30%). A slight overestimation was found at points 2, 4, and 5 (<30%) and 10 and 11 (50%), while underestimation was observed at points 1, 3, and 7. The highest difference was observed at rural site 1, which could be related with very low participation of Cu in the total metal content at this site (proved by ICP-MS method; Fig. 5); therefore, in SEM-EDX analyses, it was easy to overlook the presence of this element (Fig. 6).

The last two charts for As and Ni were not very consistent between methods. In the case of As, the comparison of SEM-EDX to ICP-MS results showed high overestimation in a few sampling points, especially 5 and 6. The situation could have been caused by the distribution of As on the spider webs not being homogeneous, and we might have randomly measured the fragments with many As-bearing particles. Conversely, underestimation was noted in the rural sites. The biggest influence on this could have a very low contribution of As at these points (about 2%), which hindered accurate measurements by SEM-EDX.

For Ni, we suggested that this element was not directly related to the smelter activity, and its presence in the web samples was

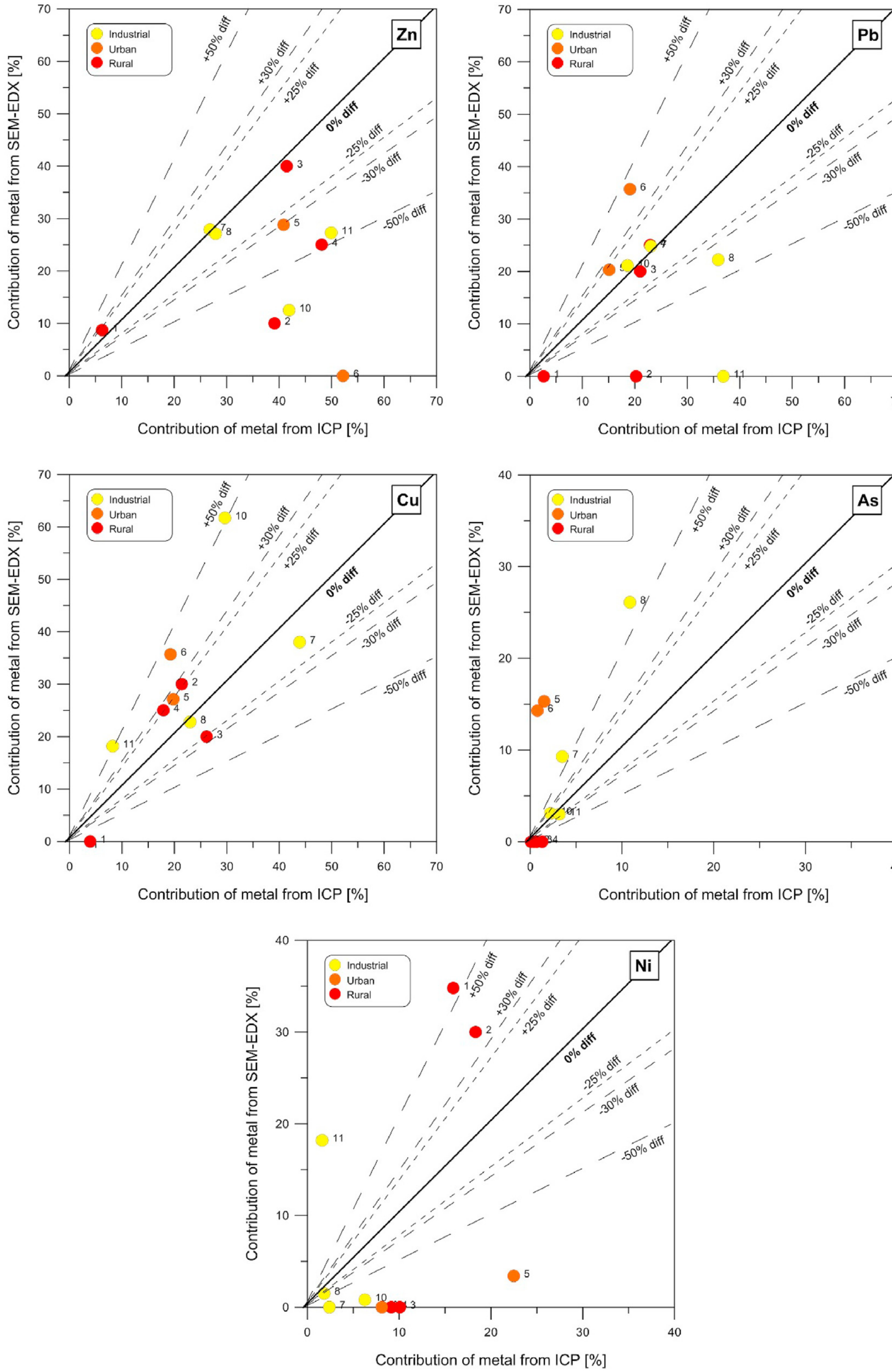

Fig. 7. The comparison of both applied methods for assessing the air pollution in the vicinity of smelter. Contribution of studied metals on spider webs in relation to ICP and SEM-EDX [% of difference].

rather accidental. This element was probably dispersed in the atmosphere, as it does not form minerals but covers different grains. These results are in agreement with experimental data presented by Kukutschová et al. (2011), who showed that particles originating from brake pad wear were in the nano-size range. In the chart, strong underestimation was noticed (points 3, 4, 5, 6, 7, and 10). In most of the sites, however, the contribution of studied elements did not exceed 10%, which, coupled with the possibility for Ni to occur in nano-size particles, caused imprecise measurements when using SEM-EDX.

To summarise, the main elements related with the activity of the smelter, such as Cu, Pb, and Zn, were detected and determined with both methods, giving the best agreement in results from industrial points 7 and 8. This suggests that the SEM-EDX method is suitable and very convenient for assessing air pollution levels, and in some cases, especially in industrial areas, it could successfully replace the more expensive ICP-MS method.

4. Conclusions

1. Based on the map of spatial distribution, the estimated range of analysed fractions $PM_{2.5}$, $PM_{2.5\text{-}10}$, and PM_{10} was about 10, 6, and 3 km, respectively. The obtained results were consistent with the dominant wind direction.
2. Larger fractions were dominated mainly by the particles derived from deflation of the Earth's crust, while smaller fractions were more diverse and composed of anthropogenic particles, originating mainly from the activity of the smelter.
3. Statistical analyses confirmed that the PTEs were strongly correlated with the finer particles, rather than with the coarse fraction. Additionally, a significant correlation between chemical and mineralogical composition was found, demonstrating that the phases and minerals were correctly recognised and divided into terrigenous and anthropogenic groups based on mineralogical composition.
4. The coupled analyses of the chemical composition and size of the PM, conducted using SEM-EDX analyser, was a good tool in identifying the possible pollutants and determining the range of its impact. However, in the case of using spider web, attention must be given to the preparation of samples for analysis, which means one should avoid folding the web.
5. The use of spider webs are not well known, but they proved again to be a perspective passive sampler, with a possible use in collecting particles of atmospheric aerosols.
6. The frequency of metal occurrence in atmospheric particles identified with the use of SEM-EDX was comparable with the results from ICP-MS recalculated into percentage contribution. Thus, the conversion of the results obtained by SEM-EDX analyses into quantitative results (ICP-MS) and vice-versa is possible, as presented in this paper.
7. We recommend application of the SEM-EDX method, especially within the area with a dominant large source of air pollution, i.e., heavily polluted industrial areas, as a cheaper and more detailed method. Apart from the information about the concentrations of studied elements, we also obtained information about grain sizes and their frequency, their shape and form, their mineralogical composition and origin. We also obtained indirect information about possible mixtures of other elements in the grains, which seemed to be more accurate than information obtained with the expensive ICP-MS technique. In the case of urban areas, with no influence of industry, the detection of pollution might be more difficult due to the occurrence of dispersed forms rather than large, easily detectable mineral forms (i.e., metallic spherules).

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.chemosphere.2021.130454.

CRediT author statement

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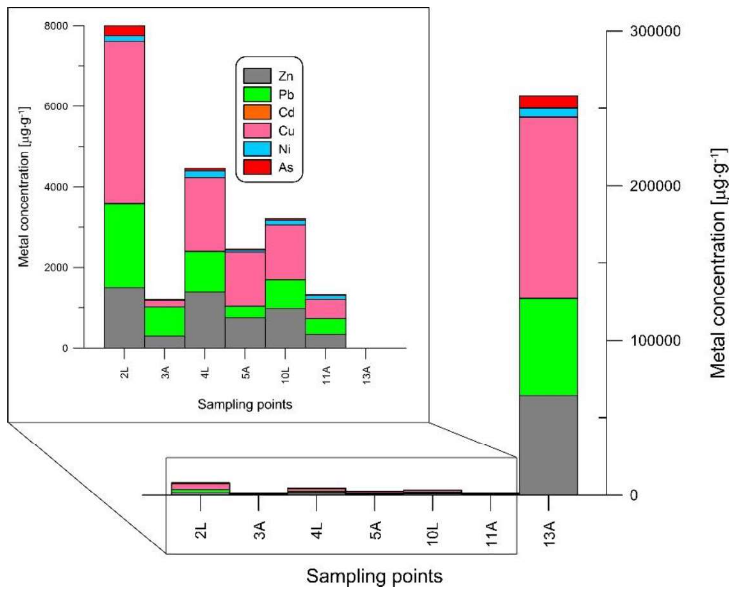
Artykuł 6

Ocena ryzyka zdrowotnego w oparciu o pierwiastki potencjalnie toksyczne zakumulowane na sieciach pajęczych połączona z charakterystyką zanieczyszczeń

Health risk assessment in the vicinity of a copper smelter: particulate matter collected on a spider web. **Agnieszka Trzyna**, Justyna Rybak, Wojciech Bartz, Maciej Górka. *Mineralogia*. 2022, vol. 53, s. 36-50.

W poniższej pracy sieci pajęcze zostały wykorzystane, jako pasywny pobornik zanieczyszczeń powietrza, w celu oszacowania ryzyka zdrowotnego, na jakie narażeni mogą być mieszkańcy miasta Legnica. Praca miała na celu rozpoznanie problemu, czy sieci pajęcze mogą być wykorzystywane w tego typu badaniach i czy można uzyskać z ich pomocą wiarygodne wyniki. W badaniach wykorzystano metodę transplantowania sieci pajęczych pająków z rodziny Agelenidae oraz Linyphiidae. Sieci wystawione były na trzymiesięczną ekspozycję w wybranych punktach, po czym zakumulowane cząsteczki zanieczyszczeń powietrza zostały przeanalizowane z wykorzystaniem SEM-EDX oraz ICP-MS. Pierwsza z metod pozwoliła na jakościowe scharakteryzowanie zakumulowanych cząstek (tj. ich składu chemicznego, kształtu oraz wielkości cząstek), podczas gdy druga z metod dostarczyła danych na temat stężeń wybranych pierwiastków występujących w pyle (As, Cu, Cd, Ni, Pb, oraz Zn; Rysunek 5). Wyniki analiz potwierdziły, że frakcja dużych cząsteczek zdominowana jest głównie przez cząsteczki naturalne, natomiast drobniejsze frakcje charakteryzowały się większym zróżnicowaniem pod kątem mineralogicznym, a ich pochodzenie przypisano źródłom antropogenicznym takim jak działalność huty miedzi oraz transport drogowy. Opierając się o wyniki analiz ilościowych wykonano obliczenia rakotwórczej i nierakotwórczej oceny ryzyka zdrowotnego, uwzględniając trzy drogi narażenia: inhalacyjną, skórną i pokarmową zarówno dla dorosłych, jak i dla dzieci. Ryzyko nierakotwórcze okazało się być wysokie (Hazard Index>1) zarówno dla dzieci, jak i dla dorosłych (dla analizowanych pierwiastków: Cu, Ni, Pb, Cd). Co więcej, ryzyko rakotwórcze pojawiło się w większości punktów pomiarowych. Przeprowadzone badania udowodniły, że osoby mieszkające na badanym obszarze narażone są na negatywny wpływ zanieczyszczeń powietrza. Dodatkowo, analiza uzyskanych wyników potwierdziła możliwość wykorzystania sieci pajęczych w biomonitoringu powietrza, a także w badaniach szacujących ryzyko zdrowotne.

Wniosek: Analiza cząsteczek zakumulowanych przez sieci pajęcze pozwala na określenie ryzyka zdrowotnego.



Rysunek 5 Skład chemiczny cząsteczek zakumulowanych na sieciach pajęczych (Trzyna et al., 2022).

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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.

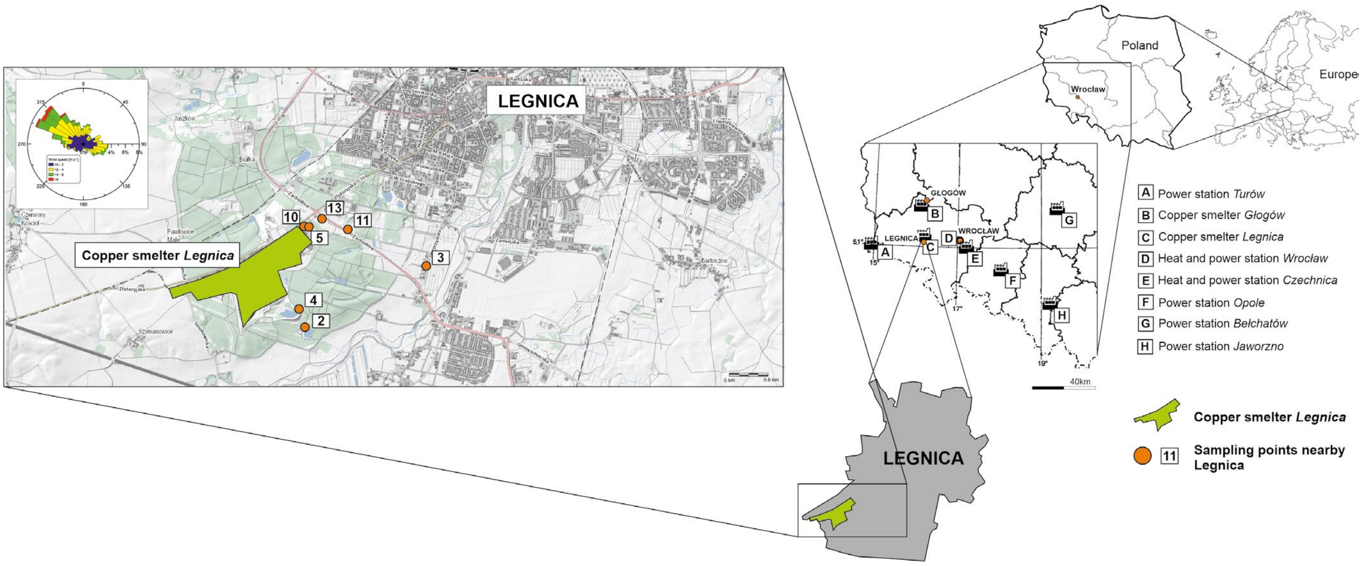

Figure 1. Location of sampling points 2-13 in the vicinity of smelter (Legnica) where spider webs belonging to Agelenidae and Linyphiidae families were taken. The source of the data is the Institute of Meteorology and Water Management - National Research Institute (IMGW-PIB). The data of the IMGW-PIB 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; Suprapur®, 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:

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

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

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

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:

$$HQ = \frac{ADD}{RfD} \tag{4}$$

$$HI = \Sigma HQ \tag{5}$$

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)

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

where:
ET - exposure time [h/d];
IUR – slope factor [µg/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	$5.67\cdot10^{-3}$- **$4.12\cdot10^{0}$**	$1.42\cdot10^{-3}$- $3.01\cdot10^{-1}$	$1\cdot57\cdot10^{-3}$- $4.1\cdot10^{-1}$	$1.62\cdot10^{-1}$- **$3.82\cdot10^{1}$**	$1.55\cdot10^{-1}$- **$2.53\cdot10^{1}$**	$6.59\cdot10^{-3}$- $7.39\cdot10^{-1}$
	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

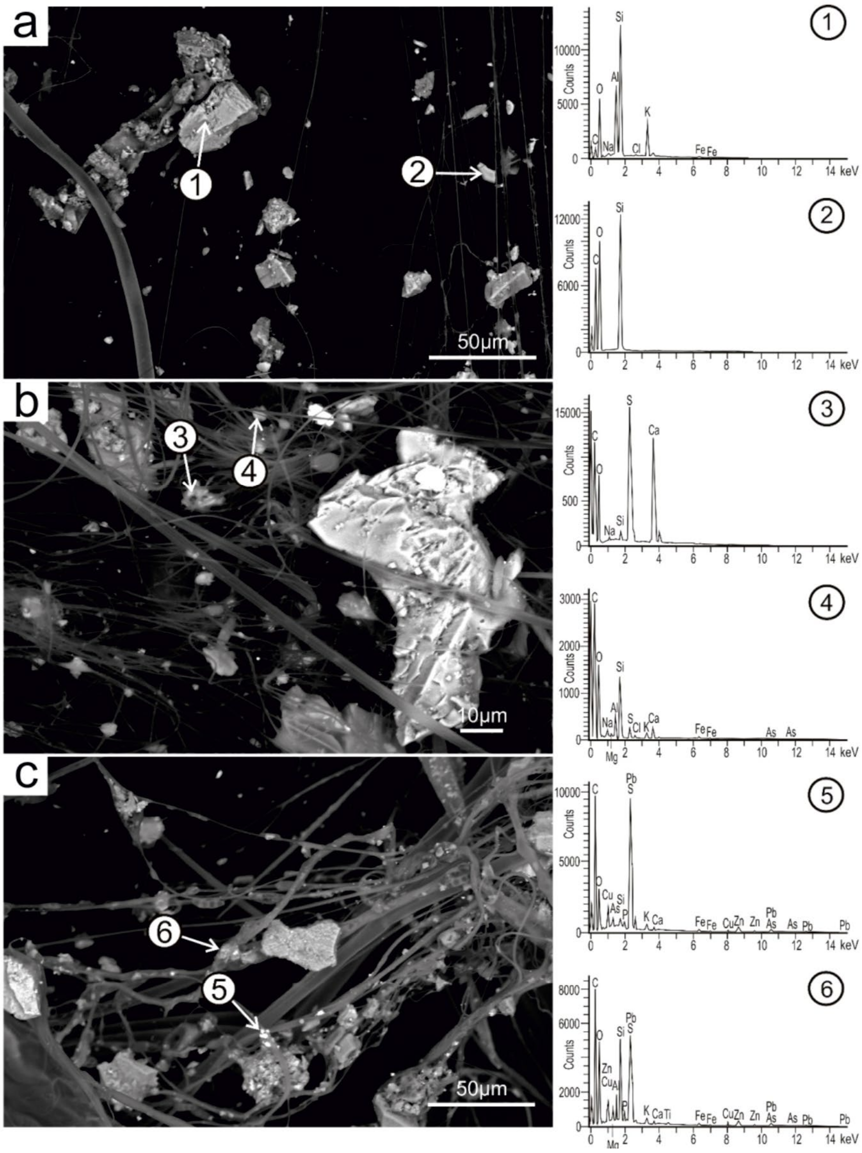

Figure 2. Backscattered electron images of spider web taken from Legnica smelter site (a) 13, (b) 5, and (c) 4 and representative Energy Dispersive X-Ray spectra. Spectrum 1 – K-feldspar, spectrum 2 – quartz, spectrum 3 – gypsum, spectrum 4 – silicate glass with As, spectrum 5 – Sulfides, spectrum 6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

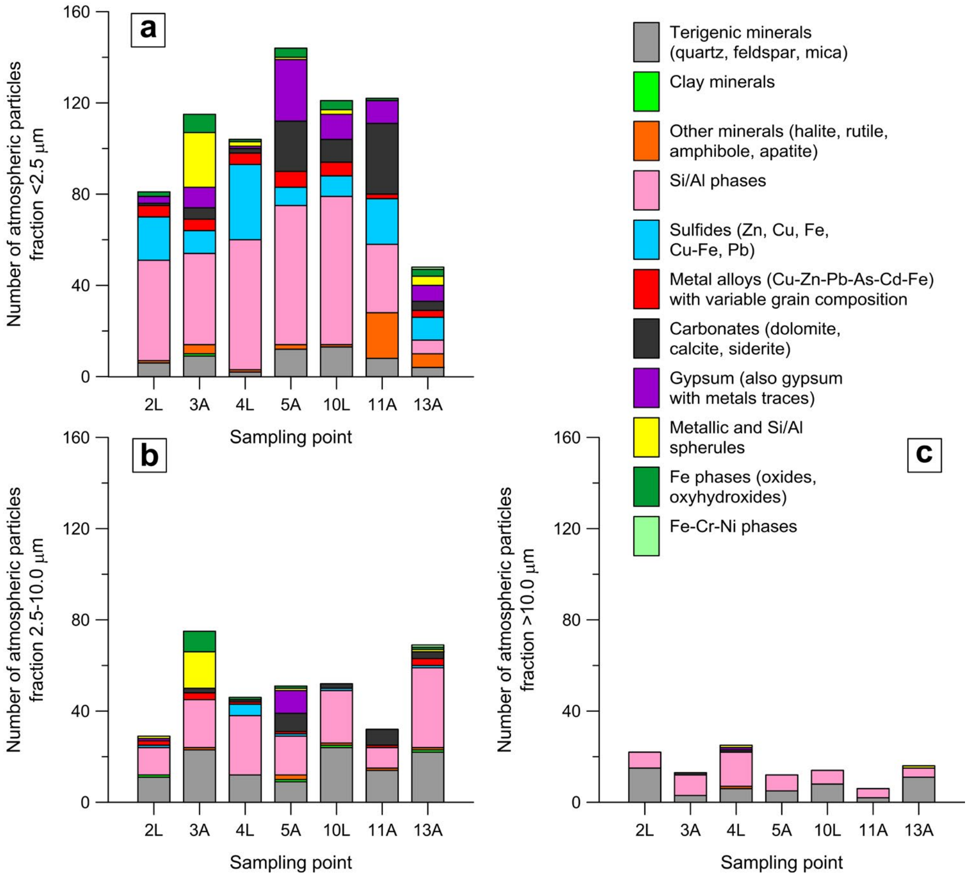

Figure 3. Mineralogical phases reported for particles deposited on spider webs collected in 2018 in the Legnica smelter vicinity. The letter A stands for Agelenidae, and L for Linyphiidae.

$$\%\text{contribution of IAP} = (100\% - (\%Q + \%OT)) \quad (7)$$

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

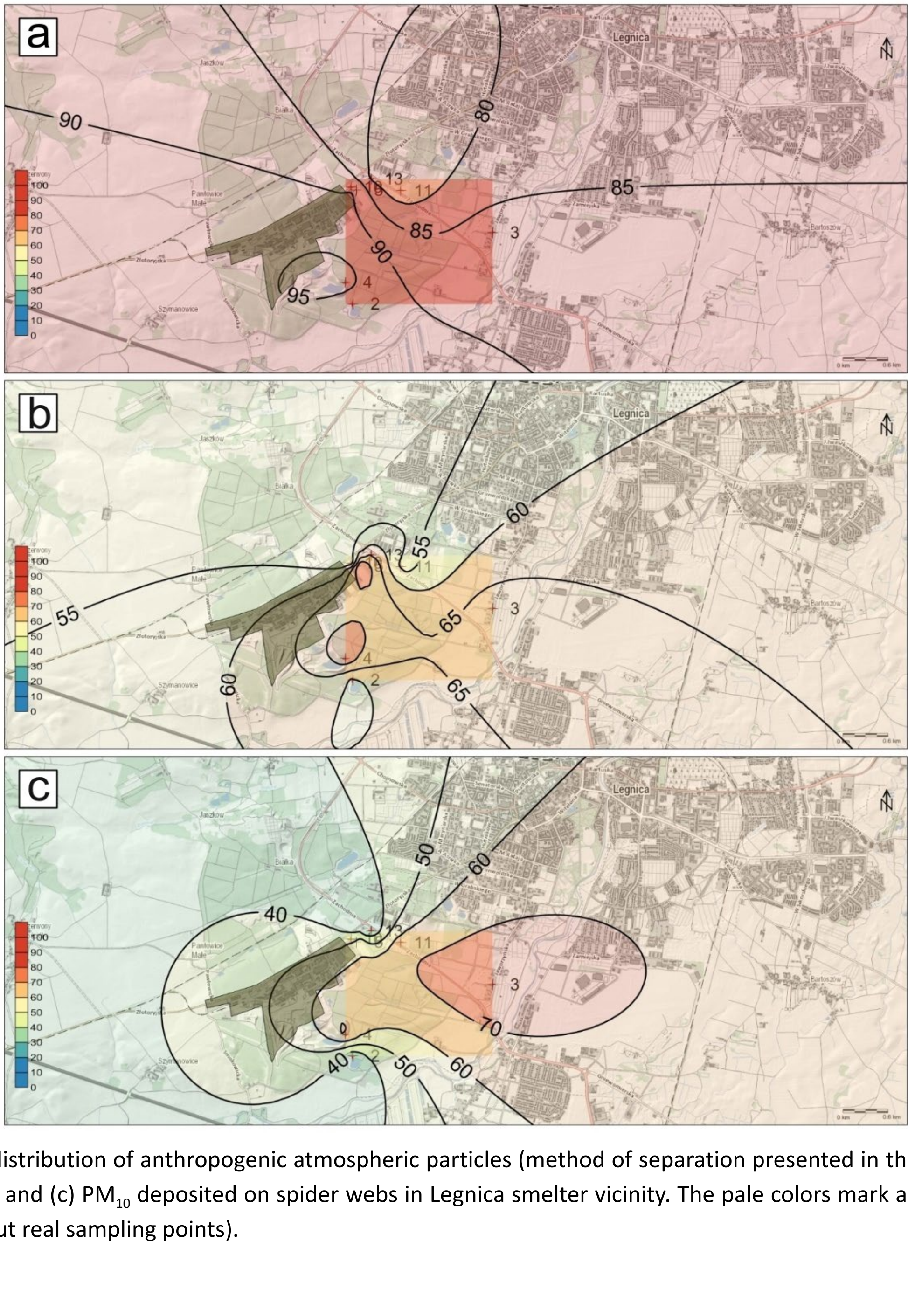

Figure 4. Spatial distribution of anthropogenic atmospheric particles (method of separation presented in the text) fraction (a) $PM_{2.5}$, (b) $PM_{2.5\text{-}10}$, and (c) PM_{10} deposited on spider webs in Legnica smelter vicinity. The pale colors mark areas with approximate data (without real sampling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

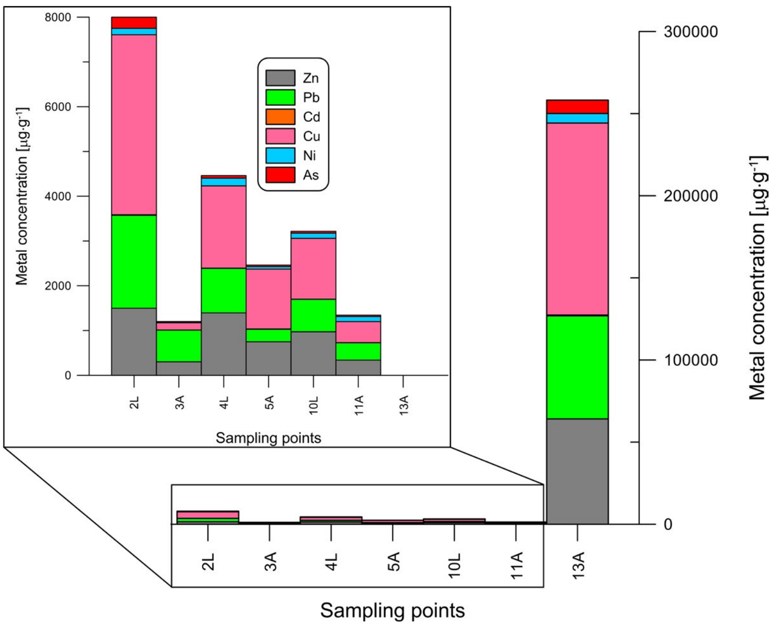

Figure 5. Chemical composition of the samples. The letter A stands for Agelenidae, and L for Linyphiidae.

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

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

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 $3.84 \cdot 10^{5}$ mg/kg for Cu, $2.11 \cdot 10^{5}$ mg/kg for Zn, and $2.06 \cdot 10^{5}$ 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 = $7.25 \cdot 10^{-4}$ mg/kg (site 3) and for Cd: ADDinh = $4.74 \cdot 10^{-4}$ mg/kg (site 10). For children, it was respectively for As: ADDinh = $1.29 \cdot 10^{-3}$ mg/kg (site 3), Cd: ADDinh = $8.51 \cdot 10^{-4}$ 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 = $3.5·10^{-2}$ (Nkansah et al. 2017), while for our studies (point 13), this value was much higher (HQing = $3.8·10^{1}$). Similarly, higher results of HI in point 13 were obtained in the case of Pb for children (HI = $6.11·10^{1}$) when compared to studies in the capital of Oman, Muscat (HI = $1.2·10^{-2}$). 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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Artykuł 7

Kontynuacja badań, dotyczących oceny ryzyka zdrowotnego w oparciu o pierwiastki potencjalnie toksyczne zakumulowane na sieciach pajęczych

Biomonitoring z wykorzystaniem sieci pajęczych – jakość powietrza i ocena narażenia zdrowotnego. **Agnieszka Trzyna**, Justyna Rybak. *Zeszyty Naukowe SGSP*. 2022, nr 82, s. 7–19.

Powyższa praca skupia się na możliwości wykorzystania sieci pajęczych w biomonitoringu powietrza z uwzględnieniem narażenia zdrowotnego, na jakie wystawieni są mieszkańcy Wrocławia. Po dwumiesięcznym czasie ekspozycji sieci pajęczych na zanieczyszczenia na obszarze miejskim przeanalizowano w nich zawartość wybranych pierwiastków (Fe, Pb, Zn), a na podstawie otrzymanych wyników obliczono narażenie zdrowotne, jakie może pojawić się poprzez ekspozycję na te pierwiastki. Obliczenia te wykonano zgodnie z modelem przedstawionym przez US EPA (US EPA, 2009) i uwzględniono trzy drogi narażenia: inhalacyjną, skórną i pokarmową zarówno dla dorosłych, jak i dla dzieci. Analiza ilościowa wskazała na stosunkowo wysokie zawartości analizowanych pierwiastków (szczególnie w przypadku Fe oraz Pb) w porównaniu do lat poprzednich. To z kolei przełożyło się na wysokie wartości wskaźników zagrożenia (HI), które wskazały, że narażenie na odnotowane stężenia może zwiększać ryzyko rozwinięcia się nienowotworowych skutków zdrowotnych wśród lokalnej ludności. Największe narażenie zaobserwowano w punktach, położonych w niedalekiej odległości od bardzo ruchliwych ulic.
Sieci pajęcze uznane zostały za niezwykle skuteczne narzędzie, które nie tylko dostarcza informacji na temat zakumulowanych pierwiastków, ale może także służyć pomocą przy ocenie narażenia zdrowotnego.

Wniosek: Analiza cząsteczek zakumulowanych przez sieci pajęcze pozwala na określenie ryzyka zdrowotnego.

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BIOMONITORING Z WYKORZYSTANIEM SIECI PAJĘCZYCH – JAKOŚĆ POWIETRZA I OCENA NARAŻENIA ZDROWOTNEGO

Abstrakt

Biomonitoring jakości powietrza z wykorzystaniem sieci pajęczych przeprowadzono we Wrocławiu w 2020 r. Po określonym czasie ekspozycji sieci przeanalizowano pod kątem zawartości pierwiastków potencjalnie toksycznych (Fe, Pb, Zn). Zważając na fakt, że otrzymane wartości były wyższe niż wartości w poprzednich latach, wykonano dodatkowo ocenę narażenia zdrowotnego, wynikającego z obecności pierwiastków potencjalnie toksycznych w powietrzu. W przypadku Fe oraz Pb całościowy wskaźnik zagrożenia był wysoki, wskazując na możliwe zagrożenie zdrowotne związane z narażeniem na te pierwiastki, natomiast wyniki dla Zn nie wskazały na istnienie takiego zagrożenia. Biomonitoring z wykorzystaniem sieci pajęczych udowodnił, że materiał ten może być z powodzeniem wykorzystywany przy oszacowaniu jakości powietrza, a analiza obecnych na sieciach pierwiastków pomaga przy ocenie zagrożenia zdrowotnego.

Słowa kluczowe: biomonitoring, jakość powietrza, sieci pajęcze, narażenie zdrowotne, Agelenidae

BIOMONITORING USING SPIDER WEBS - AIR QUALITY AND HEALTH EXPOSURE ASSESSMENT

Abstract

Air quality biomonitoring was conducted with the use of spider webs in Wrocław in 2020. After the specified exposure time, the webs were analyzed in order to determine the content of potentially toxic elements (Fe, Pb, Zn). Due to the fact that the obtained concentrations were higher than values recorded in previous years, an additional assessment of health hazard, resulting from the presence of potentially toxic elements in the air, was performed. In the case of Fe and Pb, the overall hazard index was found to be high, indicating the possible existence of a health hazard associated with exposure to these elements, while the results for Zn did not point to such a hazard.

Biomonitoring with the use of spider webs has proven that this material can be successfully used in air quality assessment, and the analysis of the elements collected on the webs can help in assessing health hazard.

Keywords: biomonitoring, air quality, spider web, health hazard, Agelenidae

1. Wstęp

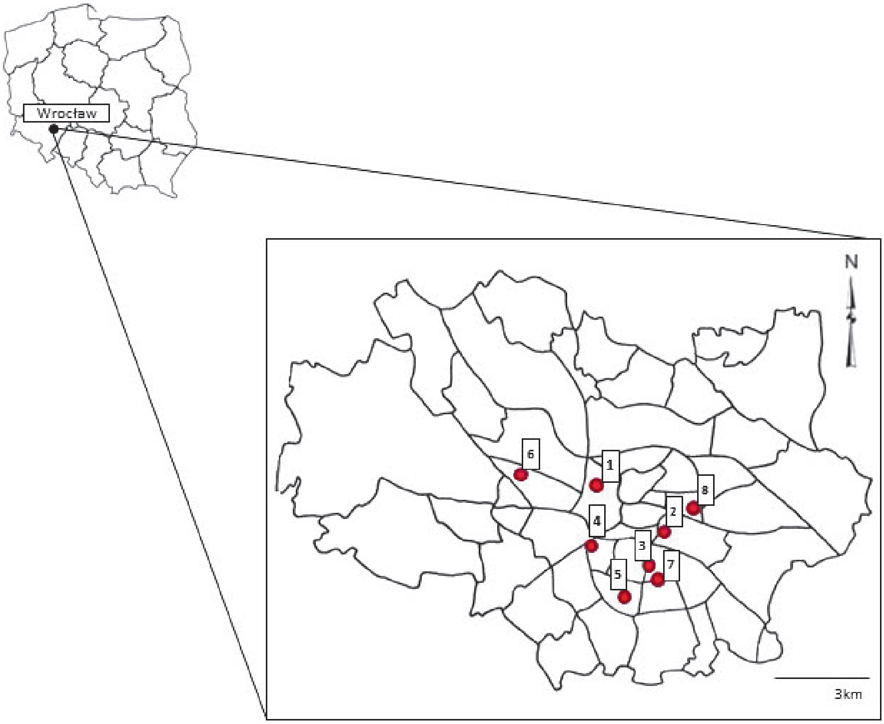
Zanieczyszczenia powietrza stanowią obecnie bardzo poważny problem dla ludzkości [1]. Problem ten dotyczy wielu miejsc na świecie, również Europy, gdzie mimo ciągłych starań jakość powietrza wciąż pozostawia wiele do życzenia [1]. Komisja Europejska podaje, że zanieczyszczenia powietrza, zaraz po zmianach klimatycznych, są dla Europejczyków jednym z największych zagrożeń środowiskowych, prowadzących do różnorakich chorób, szczególnie chorób układu oddechowego [2]. Co więcej, zanieczyszczenia powietrza zewnętrznego (głównie drobny pył zawieszony $PM_{2,5}$) uznane zostały przez Międzynarodową Agencję Badań nad Rakiem za główny czynnik prowadzący do powstawania komórek rakowych, a ostatecznie śmierci [3]. Dlatego też tak ważne jest prowadzenie badań dotyczących oceny jakości powietrza. Standardowy monitoring powietrza, mimo że dostarcza bardzo precyzyjnych wyników, może być w niektórych przypadkach niedostępny ze względu na koszty czy konieczność posiadania wykwalifikowanych pracowników, zdolnych do obsługi profesjonalnego sprzętu. To wszystko powoduje ciągłe poszukiwanie tanich, łatwo dostępnych narzędzi, które z powodzeniem mogłyby dostarczyć informacji na temat aktualnych zanieczyszczeń powietrza. Bardzo popularnym narzędziem jest biomonitoring, który polega na wykorzystaniu organizmów żywych lub ich produktów do oceny stanu środowiska [4]. W badaniach dotyczących powietrza najczęściej wykorzystywanymi organizmami są mchy i porosty [5–7], a także liście i igły drzew [8–10]. W ostatnich czasach naukowcy testują również sieci pajęcze, które, będąc pasywnym próbnikiem odpowiedzialnym za kumulację zanieczyszczeń, również mogą dostarczyć wielu cennych informacji na temat jakości powietrza [11–14]. W badaniach biomonitoringowych z wykorzystaniem sieci pajęczych najczęściej analizuje się pierwiastki potencjalnie toksyczne [12, 15], nieco rzadziej pojawiają się badania nad wielopierścieniowymi węglowodorami aromatycznymi (WWA) [16, 17]. Dodatkowo, dwukrotnie analizowano sieci pajęcze pod kątem podatności magnetycznej, a wyniki potwierdziły ich użyteczność w monitoringu magnetycznym [18, 19]. To wszystko wskazuje, że sieć pajęcza ma potencjał jako dobry bioindykator. Co więcej, materiał ten jest tani, łatwo dostępny, a proces poboru próbek nie generuje dodatkowych odpadów. Atutem jest też możliwość założenia laboratoryjnej hodowli pająków, która dostarcza czystych sieci pajęczych z możliwością transplantowania ich na obszar badań [20]. Spośród wielu różnych rodzin pająków najprzydatniejsze okazują się pająki z rodziny Agelenidae, których sieci są duże, gęste, zbudowane z nieregularnie ułożonych grubych nici, dzięki czemu kumulacja cząstek zanieczyszczeń na ich powierzchni jest możliwa. Co więcej, pająki z tej rodziny występują powszechnie i budują swoje sieci w miejscach umożliwiających ich łatwe pobranie, co stanowi przewagę nad podobnymi w budowie sieciami innych pająków [21]. Dodatkowo, metoda transplantacji takich sieci pozwala na dokładne określenie czasu ekspozycji, co w przypadku poboru próbek *in situ* jest dużo trudniejsze lub niemożliwe.

Celem artykułu jest pokazanie użyteczności transplantowanych sieci pajęczych przy jakościowej ocenie stanu powietrza. By spełnić to zadanie, przeanalizowano zawartość wybranych pierwiastków potencjalnie toksycznych, skumulowanych na sieciach pajęczych, a także oceniono narażenie zdrowotne, jakie może występować przy ekspozycji na te pierwiastki w celu oszacowania wpływu tych zanieczyszczeń na zdrowie człowieka. Hipoteza badawcza zakłada, że sieci pajęcze mogą być użytecznym bioindykatorem, pozwalającym również na dostarczenie cennych informacji na temat wpływu cząstek zanieczyszczeń na zdrowie człowieka.

2. Obszar badań

Badania przeprowadzone zostały we Wrocławiu w województwie dolnośląskim. Wrocław jest dużym miastem o zaludnieniu ponad 600 000 mieszkańców. Zgodnie z raportami przedstawianymi przez Główny Inspektorat Ochrony Środowiska (GIOŚ) pył zawieszony (PM_{10}) w latach 2016–2020 w całej strefie dolnośląskiej przekraczał zarówno dopuszczalny poziom średnioroczny, jak i 24-godzinny. W przypadku $PM_{2,5}$ wyniki plasowały się w okolicy górnego progu [22]. Raport ten wskazuje więc na poważny problem dotyczący jakości powietrza, z jakim mierzy się ten rejon. W samym mieście nie ma żadnego przemysłu ciężkiego, a za większość zanieczyszczeń odpowiada natężony ruch drogowy, miejska elektrociepłownia oraz niska emisja w sezonie grzewczym [23]. Oprócz emisji lokalnej znaczący wpływ ma także napływ zanieczyszczeń z pozostałych obszarów Polski oraz Europy [24]. W przypadku emisji pyłów PM_{10} oraz $PM_{2,5}$ w województwie dolnośląskim największy udział ma sektor komunalno-bytowy, sięgając odpowiednio 69% i 86%. Pozostały wkład mają: transport drogowy, głównie związany ze ścieraniem się opon i nawierzchni dróg oraz unoszeniem zanieczyszczeń z powierzchni dróg, emisja punktowa oraz hałdy i okoliczne wyrobiska kopalni odkrywkowych.

Próbki sieci pajęczych umieszczono w ośmiu miejscach we Wrocławiu, jak przedstawiono na mapie (rys. 1). Próbki 3 oraz 5 umieszczone zostały w parkach miejskich (Park Andersa oraz Park Południowy), pozostałe próbki ulokowano w miejscach o dość dużym natężeniu ruchu samochodowego (1 – ul. Legnicka, 2 – ul. Kościuszki, 4 – ul. Krucza, 6 – ul. Metalowców, 7 – ul. Armii Krajowej, 8 – pl. Grunwaldzki).



Rys. 1. Lokalizacja punktów pomiarowych
Źródło: opracowanie własne

2.1. Warunki pogodowe

Rok 2020 zaliczany jest do ekstremalnie ciepłych, biorąc pod uwagę średnią dla całego obszaru Polski. W 2020 r. średnia temperatura w Polsce wynosiła 9,9°C, czyli była aż o 1,6°C wyższa niż w poprzednich latach [25]. Najcieplejszym miesiącem był sierpień, a najzimniejszym grudzień. W styczniu i w lutym zaobserwowano temperatury znacznie wyższe w porównaniu z normą klimatologiczną, odpowiednio o 3,7°C i 4,6°C. Pod względem opadów rok 2020 nie odbiegał od normy, a roczne opady na obszarze Polski wyniosły 104,4% normy wieloletniej (1981–2010) [24].

Wrocław w 2020 r. był najcieplejszym miastem w Polsce ze średnią temperaturą roczną równą 11,1°C. W nizinnej części województwa dolnośląskiego suma opadów atmosferycznych w 2020 r. wynosiła od 500 mm, podczas gdy w rejonach górskich suma sięgała do 1000 mm. Zarówno luty, jak i czerwiec we Wrocławiu były rekordowe pod względem sumy opadów. W 2020 r. na terenie województwa dolnośląskiego przeważały wiatry zachodnie oraz południowo-zachodnie. Najmniejszy udział miały wiatry z kierunków północno-wschodnich [24].

3. Metodyka

3.1. Biomonitoring z wykorzystaniem sieci pajęczych

Biomonitoring z wykorzystaniem sieci pajęczych przeprowadzono w 2020 r. (01.01–01.03) we Wrocławiu (rys. 1). W pracy wykorzystano sieci pająków należących do rodziny lejkowcowatych (Agelenidae), tj. *Eratigena atrica* (C.L. KOCH, 1843) oraz *Agelena labyrinthica* (CLERCK, 1757). Pająki te mogą pojawiać się w kątach mieszkań, w piwnicach, a także w niskich zaroślach. Sieci budowane przez lejkowcowate mają kształt płachty utkanej z gęsto położonych grubych nici sieci, wraz z lejkiem, w którym chowa się pająk [26]. Co najważniejsze, pająki z tej rodziny nie zjadają swoich sieci, co umożliwia pozyskiwanie czystej sieci do transplantacji, a także ułatwia pobór reprezentatywnych próbek *in situ*.

W tej pracy próbki sieci pajęczych pobrane zostały z laboratoryjnej hodowli pająków, co zapewniło czystość sieci przed ekspozycją oraz możliwość dokładnego określenia czasu ekspozycji próbek w terenie. Próbki sieci z laboratorium były poprzednio analizowane pod kątem zawartości pierwiastków potencjalnie toksycznych, a wyniki pokazały, że wartości te były pomijalne. Sieć utkana w terrariach przez lejkowcowate została manualnie rozciągnięta na plastikowych szalkach Petriego, na których następnie przetransportowano ją w teren badań i przytwierdzono do wybranej powierzchni klejem. Szalki umieszczane były na wysokości około 1,5 m i pozostawione na okres dwóch miesięcy na opad zanieczyszczeń (01.01.2020–01.03.2020). Po czasie ekspozycji próbki zostały zebrane z wykorzystaniem szklanej bagietki i przechowywane w sterylnych szklanych fiolkach aż do czasu analizy. Próbki kondycjonowano przez 24 h (temp.: 20 ± 2°C, wilg.: 40 ± 5%), po czym zważono je trzykrotnie w warunkach temperaturowych 20 ± 2°C i 40 ± 5% wilgotności powietrza. Do ważenia próbek wykorzystano wagę Radwag AS 60/C/2 (minimalna masa 1 mg, dokładność 0,01 mg, powtarzalność 0,04 mg).

3.2. Analiza pierwiastków na sieciach

Mineralizację próbek oraz analizę mineralizatów przeprowadzono w Instytucie Inżynierii Środowiska i Biotechnologii na Uniwersytecie Opolskim. Próbki mineralizowano, wykorzystując zamknięty system mikrofalowy Speedwave Four firmy BERGHOF, DE. Do mineralizacji użyto mieszaniny 5 cm^3 HNO_3 (65% Merck) oraz 3 cm^3 H_2O_2. Proces przeprowadzono dwukrotnie w temperaturze 220°C przez 20 minut, tak by zapewnić całkowitą mineralizację pyłu zgodnie z [27]. Stężenia Pb, Zn oraz Fe określono na sieciach pajęczych, wykorzystując atomową spektrometrię absorpcyjną z atomizacją w płomieniu (FAAS) typ iCE 3500 (seria 3000) firmy Thermo Scientific, USA. Spektrometr iCE 3500 charakteryzuje się następującymi limitami detekcji: Pb = 0,0130 mg/dm^3, Zn = 0,0033 mg/dm^3, Fe = 0,0043 mg/dm^3.

3.3. Narażenie zdrowotne

Narażenie zdrowotne, wynikające z obecności pierwiastków potencjalnie toksycznych (Fe, Zn, Pb) w powietrzu, zostało policzone zgodnie z modelem przedstawionym przez US EPA [28]. W celu oszacowania potencjalnego narażenia zarówno dla dorosłych, jak i dla dzieci, wzięto pod uwagę trzy różne możliwe drogi penetracji dla powyższych pierwiastków: droga doustna, wziewna i skórna. Wykorzystując wzory przedstawione poniżej, obliczono ilość potencjalnie szkodliwej substancji, na jaką narażony byłby człowiek w ciągu jednego dnia w przeliczeniu na 1 kg masy ciała [29].

$$ADD_{ing} = C \times \frac{IngR \times EF \times ED}{BW \times AT}$$

$$ADD_{inh} = C \times \frac{InhR \times EF \times ED}{PEF \times BW \times AT} \times 10^{6}$$

$$ADD_{derm} = C \times \frac{SL \times SA \times ABS \times EF \times ED}{BW \times AT}$$

gdzie:
C (ang. *concentration of contaminant in medium*) – średnie stężenie pierwiastka potencjalnie toksycznego [mg/kg];
IngR (ang. *ingestion rate*) – wartość dziennego przypadkowego spożycia pyłu [mg/d];
InhR (ang. *inhalation rate*) – wielkość dobowej wentylacji płuc [m^3/d];
EF (ang. *exposure frequency*) – częstotliwość narażenia [dni/rok];
ED (ang. *exposure duration*) – okres życia narażonego dziecka/dorosłego [rok];
BW (ang. *body weight*) – średnia masa ciała [kg];
AT (ang. *averaging time*) – uśredniony czas narażenia [dni];
PEF (ang. *particle emission factor*) – współczynnik emisji cząstek [m^3/kg];
SL – współczynnik przylegania cząstek pyłu do skóry [mg/cm^2 x d];
SA – powierzchnia skóry w kontakcie z pyłem [cm^2];
ABS – współczynnik wchłaniania dermalnego.

Ocenę ryzyka zdrowotnego policzono na podstawie oszacowania wartości HQ (ang. *hazard quotient*), czyli ilorazu zagrożenia, zgodnie ze wzorem poniżej:

$$HQ = \frac{ADD}{RfD}$$

gdzie:
HQ – iloraz zagrożenia:
HQ < 1 – brak lub niewielkie ryzyko wystąpienia negatywnych efektów w populacji narażonej,

HQ ≥ 1 – ryzyko wystąpienia negatywnych efektów zdrowotnych w populacji narażonej jest prawdopodobne;
ADD (ang. *Potential Average Daily Dose*) – potencjalna średnia dzienna dawka [ng/kg/dzień];
RfD – dawka referencyjna, przyjęta na poziomie: RfD_{ing} = 7000 ng/kg/d, RfD_{inh} = = 8000 ng/kg/d, RfD_{derm} = 7000 ng/kg/d dla Fe, RfD_{ing} = 3500 ng/kg/d, RfD_{inh} = 3520 ng/kg/d, RfD_{derm} = 525 ng/kg/d dla Pb oraz RfD_{ing} = = 300 000 ng/kg/d, RfD_{inh} = 300 000 ng/kg/d, RfD_{derm} = 60 000 ng/kg/d dla Zn.

Końcowo obliczono wskaźnik zagrożenia HI (ang. *hazard index*), który jest sumą wpływu analizowanej substancji we wszystkich drogach narażenia.

4. Wyniki

4.1. Zawartość pierwiastków

Monitoring z wykorzystaniem sieci pajęczych pokazał, że zawartość wybranych pierwiastków na sieciach jest zróżnicowana. Największe stężenia odnotowano dla Fe (średnia: 11932 ± 1679 mg/kg), którego zawartość wahała się od 9779 mg/kg do 14716 mg/kg, kolejno Pb w zakresie od 946 mg/kg do 8731 mg/kg (średnia: 2935 ± ± 2563 mg/kg), a na końcu Zn z minimum w 994 mg/kg, a maksimum 2443 mg/kg (średnia: 1368 ± 482 mg/kg).

4.2. Narażenie zdrowotne

Narażenie zdrowotne zależne jest od konkretnej dawki, jaka potencjalnie mogła zostać przyjęta przez osobę dorosłą lub dziecko. Aby oszacować narażenie zdrowotne, obliczono więc w pierwszej kolejności potencjalne średnie dzienne dawki (ADD) dla trzech różnych dróg narażenia: doustną (ADD_{ing}), inhalacyjną (ADD_{inh}), dermalną (ADD_{derm}) (tab. 1). Wyniki pokazały zróżnicowanie dawek w zależności od wieku narażonej osoby (dzieci/dorośli) oraz metalu, na który mogli zostać narażeni. W obydwu grupach największe ilości pierwiastków potencjalnie toksycznych mogą być przyswajane drogą doustną, następnie dermalną, a najmniejsze ilości drogą inhalacyjną (tab. 1).

Biorąc pod uwagę referencyjne dawki dla analizowanych metali, obliczono wskaźnik zagrożenia (HI) (tab. 2). W przypadku cynku, zarówno dla dorosłych, jak i dla dzieci, HQ nie przekraczał wartości 1, a więc nie ma podstaw do stwierdzenia, że istnieje ryzyko wystąpienia negatywnych efektów zdrowotnych w populacji narażonej. Jak się okazuje, Pb może stanowić zagrożenie dla dzieci w momencie przypadkowego

Tab. 1. Wyliczone potencjalne średnie dzienne dawki (ADD, zakresy: minimum--maksimum) dla różnych dróg przyswajania (ng/kg/d)

		Pb	Zn	Fe
Dorośli	ADD_{ing}	$1,3 \times 10^{3}$–$1,2 \times 10^{4}$	$1,4 \times 10^{3}$–$3,4 \times 10^{3}$	$1,4 \times 10^{4}$–$2,1 \times 10^{4}$
	ADD_{inh}	$9,6 \times 10^{-2}$–$8,9 \times 10^{-1}$	$1,0 \times 10^{-1}$–$2,5 \times 10^{-1}$	$1,0 \times 10^{0}$–$1,5 \times 10^{0}$
	ADD_{derm}	$2,7 \times 10^{1}$–$2,5 \times 10^{2}$	$2,8 \times 10^{1}$–$6,9 \times 10^{1}$	$2,8 \times 10^{2}$–$4,1 \times 10^{2}$
Dzieci	ADD_{ing}	$3,1 \times 10^{3}$–$2,9 \times 10^{4}$	$3,3 \times 10^{3}$–$8,0 \times 10^{3}$	$3,2 \times 10^{4}$–$4,8 \times 10^{4}$
	ADD_{inh}	$1,7 \times 10^{-1}$–$1,6 \times 10^{0}$	$1,8 \times 10^{-1}$–$4,4 \times 10^{-1}$	$1,8 \times 10^{0}$–$2,6 \times 10^{0}$
	ADD_{derm}	$1,7 \times 10^{1}$–$1,6 \times 10^{2}$	$1,8 \times 10^{1}$–$4,5 \times 10^{1}$	$1,8 \times 10^{2}$–$2,7 \times 10^{2}$

Źródło: opracowanie własne

Tab. 2. Wyliczone średnie wartości ilorazu zagrożenia (HQ, zakresy: minimum--maksimum) oraz wskaźnika zagrożenia (HI, zakresy: minimum-maksimum) dla różnych dróg przyswajania

		Pb	Zn	Fe
Dorośli	HQ_{ing}	$4,0 \times 10^{-1}$–$3,5 \times 10^{0}$	$3,0 \times 10^{-6}$–$1,4 \times 10^{-5}$	$2,0 \times 10^{0}$–$3,0 \times 10^{0}$
	HQ_{inh}	$2,7 \times 10^{-5}$–$2,5 \times 10^{-4}$	$2,2 \times 10^{-10}$–$1,0 \times 10^{-9}$	$1,2 \times 10^{-4}$–$1,9 \times 10^{-4}$
	HQ_{derm}	$1,0 \times 10^{-1}$–$5,0 \times 10^{-1}$	$3,0 \times 10^{-7}$–$1,4 \times 10^{-6}$	$3,9 \times 10^{-2}$–$5,9 \times 10^{-2}$
	HI	$4,0 \times 10^{-1}$–$4,0 \times 10^{0}$	$3,3 \times 10^{-6}$–$1,5 \times 10^{-5}$	$2,0 \times 10^{0}$–$3,0 \times 10^{0}$
Dzieci	HQ_{ing}	$9,0 \times 10^{-1}$–$8,2 \times 10^{0}$	$7,1 \times 10^{-6}$–$3,3 \times 10^{-5}$	$4,6 \times 10^{0}$–$6,9 \times 10^{0}$
	HQ_{inh}	$4,8 \times 10^{-5}$–$4,5 \times 10^{-4}$	$6,0 \times 10^{-7}$–$1,5 \times 10^{-6}$	$2,2 \times 10^{-4}$–$3,3 \times 10^{-4}$
	HQ_{derm}	$3,3 \times 10^{-2}$–$3,0 \times 10^{-1}$	$3,0 \times 10^{-4}$–$7,5 \times 10^{-4}$	$2,6 \times 10^{-2}$–$3,9 \times 10^{-2}$
	HI	$9,0 \times 10^{-1}$–$8,5 \times 10^{0}$	$3,2 \times 10^{-4}$–$7,6 \times 10^{-4}$	$4,6 \times 10^{0}$–$7,0 \times 10^{0}$

Źródło: opracowanie własne

spożycia (HQing > 1 we wszystkich punktach oprócz nr 4), a także dla dorosłych, co pokazują wyniki HQing z punktów 3, 7 i 8. Ostatni z badanych pierwiastków (Fe), podobnie do Pb, wskazuje na możliwe zagrożenie w przypadku doustnego spożycia pyłu (HQing > 1 we wszystkich lokalizacjach dla obydwu rozważanych grup).

5. Dyskusja

Biomonitoring z wykorzystaniem sieci pajęczych nie pierwszy raz udowadnia, że jest metodą użyteczną i pozwala szacunkowo określić jakość powietrza na badanym obszarze. Analiza pierwiastków potencjalnie toksycznych pokazała, że zawartość metali na sieci jest zróżnicowana. Porównując otrzymane wyniki z wynikami z lat poprzednich, można zaobserwować, że zawartość kumulowanych na sieciach pierwiastków wzrosła. Dla przykładu, w pracy Rybak [15] średnie wartości dla Wrocławia po sześćdziesięciodniowym biomonitoringu wynosiły odpowiednio: Fe = 4116 mg/g, Zn = 1477 mg/g, a Pb = 173 mg/g. Z aktualnych danych wynika, że pomimo jednakowego okresu ekspozycji na zanieczyszczenia, zawartości pierwiastków potencjalnie toksycznych są dużo większe (dla Fe = 11932 ± 1679 mg/g oraz Pb = 2935 ± 2563 mg/g), natomiast wartości Zn są w obu pracach dość podobne (obecnie: Zn = 1368±482 mg/g, Zn = 1477 mg/g dla 2013 roku). Czynnik powodujący zróżnicowanie może być związany z miesiącem ekspozycji. W przypadku aktualnych badań ekspozycja na zanieczyszczenia miała miejsce w zimie, natomiast w pracy Rybak [15] ekspozycja była w miesiącu letnim. Zimą zazwyczaj odnotowywane są problemy z jakością powietrza, a zawartość pyłu zawieszonego jest zdecydowanie wyższa niż w sezonie letnim. Największe średnie zawartości odnotowano dla żelaza, którego obecność w pyle zawieszonym może być powiązana ze spalaniem paliw kopalnych [30], procesami przemysłowymi i metalurgicznymi [31], a także z emisją z transportu (m.in. zużycie opon [32] czy zużycie hamulców [33]). Obecność atmosferycznego Pb, mimo używania benzyny bezołowiowej, wciąż w głównej mierze wiązana jest z emisją z pojazdów wykorzystujących paliwo [34], a odkąd zaczęto używać benzyny bezołowiowej, Zn stał się nowym wskaźnikiem emisji pochodzącej z transportu [35]. Związane jest to w głównej mierze z tym, że Zn obecny jest w paliwie, smarach silnikowych czy w dodatkach przeciwzużyciowych w klockach hamulcowych [36].

Prace przeprowadzone na terenie Polski, dotyczące narażenia zdrowotnego, związanego z obecnością pierwiastków potencjalnie toksycznych w pyle zawieszonym, wskazują na istniejące zagrożenie [37, 38]. Wyniki otrzymane w tej pracy pokazały, że narażenie zdrowotne, na jakie wystawieni mogą być mieszkańcy Wrocławia, jest w szczególności związane z obecnością Pb oraz Fe w powietrzu. Generalnie obecność Fe w powietrzu ma negatywny wpływ na zdrowie człowieka, co powiązane jest z uszkadzaniem DNA poprzez stres oksydacyjny, wywołany generowaniem wolnych rodników i reaktywnych form tlenu [39]. Z kolei w przypadku Pb nawet narażenie na niską zawartość tego pierwiastka może prowadzić do uszkodzenia systemu nerwowego [40], a także zwiększyć ryzyko dysfunkcji poznawczych [41]. Mając to na uwadze, zawartość pierwiastków potencjalnie toksycznych we Wrocławiu powinna być ciągle monitorowana i podlegać ocenie. Wyniki pokazują, że szczególnie problematyczne może być narażenie na pierwiastki potencjalnie toksyczne drogą doustną, co zostało potwierdzone przez wysoki wskaźnik HQ dla Fe (średnia: HQ = 2,4 dla dorosłych, HQ = 5,6 dla dzieci) oraz nieco niższy, ale wciąż świadczący o ryzyku wskaźnik HQ dla Pb (średnia: HQ = 1,2 dla dorosłych, HQ = 2,8 dla dzieci).

6. Wnioski

Analiza sieci wystawionych na zanieczyszczenia we Wrocławiu pokazała dość wysokie zawartości wybranych pierwiastków (szczególnie Fe oraz Pb), a wyliczenia związane z narażeniem zdrowotnym wskazują, że narażenie na takie stężenia może zwiększać ryzyko wystąpienia negatywnych efektów zdrowotnych w populacji narażonej, zarówno wśród dorosłych, jak i dzieci. Największe narażenie zaobserwowano w punktach 1 oraz 7 zarówno dla dzieci, jak i dla dorosłych. Punkty te były punktami położonymi w niewielkiej odległości od ruchliwych ulic (ul. Legnicka oraz ul. Armii Krajowej), więc z uwagi na wzmożony ruch samochodowy wynik narażenia zdrowotnego nie jest zaskakujący. W zależności od sposobu kontaktu z substancjami potencjalnie szkodliwymi iloraz zagrożenia był zmienny, a uśrednione wartości kształtowały się w następujący sposób: HQing > HQderm > HQinh dla obu grup wiekowych. Całościowy wskaźnik zagrożenia był wysoki w przypadku Fe oraz Pb, wskazując na możliwe zagrożenie zdrowotne związane z narażeniem na te pierwiastki. Badania udowadniają, że sieci pajęcze, z racji na swoją szeroką dostępność oraz łatwość i niski koszt pozyskania materiału, uznane mogą być za skuteczne narzędzie biomonitoringowe. Wykorzystanie ich przy ocenie jakości powietrza może dostarczyć informacji na temat zarówno ilości zawartych pierwiastków potencjalnie toksycznych, jak i narażenia zdrowotnego.

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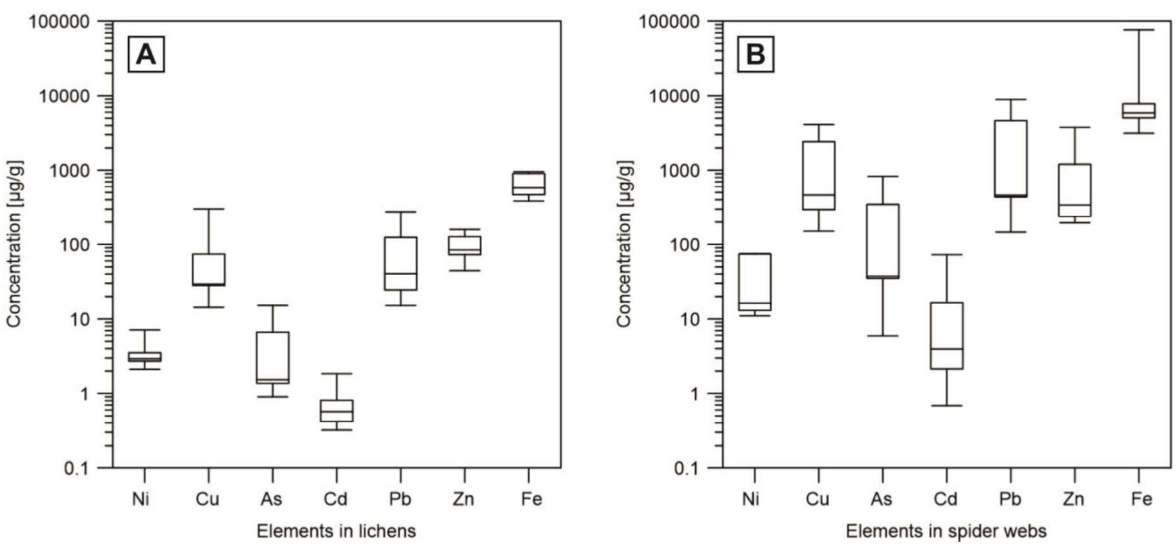
Artykuł 8

Porównanie kumulacji pierwiastków potencjalnie toksycznych przez sieci pajęcze z wynikami z aktywnego monitoringu powietrza ($PM_{2,5}$)

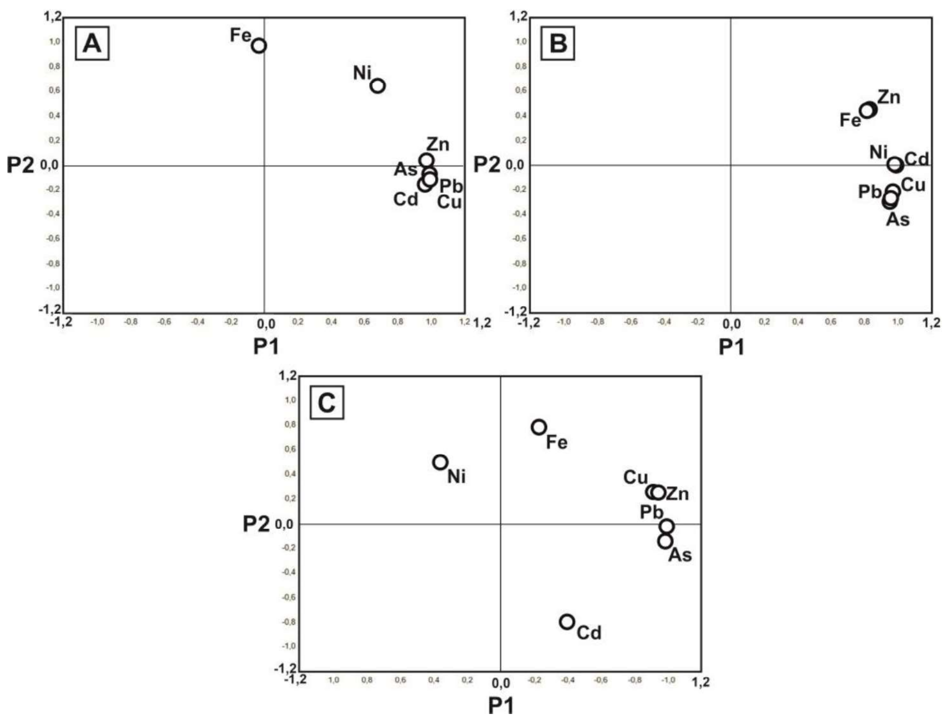
Comparison of active and passive methods for atmospheric particulate matter collection: From case study to a useful biomonitoring tool. **Agnieszka Trzyna**, Justyna Rybak, Maciej Górka, Tomasz Olszowski, Joanna A. Kamińska, Tomasz Węsierski, Małgorzata Majder-Łopatka. *Chemosphere*. vol. 334, art. 139004, s. 1-11.

Niniejsza praca porównawcza dotyczy zestawienia zanieczyszczeń zakumulowanych na sieciach pajęczych pająków z rodziny Agelenidae z wynikami z monitoringu aktywnego z wykorzystaniem pyłomierza. Dodatkowo część pracy dotyczy także ilościowego porównania akumulacji zanieczyszczeń metalonośnych na sieciach pajęczych z akumulacją przez porosty. Badania przeprowadzone zostały na obszarze miasta Legnica (w okolicy huty miedzi Legnica i skrzyżowania dróg A4/S3), gdzie wyznaczono osiem punktów pomiarowych dla sieci pajęczych oraz porostów i jeden punkt pomiarowy, w którym umieszczony został pyłomierz. We wszystkich pobranych próbkach oznaczono następujące pierwiastki: Zn, Pb, Cu, Cd, Ni, As, Fe. Bezpośrednie porównanie stężeń tych pierwiastków odnotowanych na sieciach pajęczych oraz w porostach potwierdziło wyniki z poprzednich badań, ukazując, że stężenia te są statystycznie różne. Co więcej, kolejny raz zaobserwowano, że sieci pajęcze akumulują dużo wyższe stężenia w porównaniu do porostów (Rysunek 6).



Rysunek 6 Stężenia wybranych pierwiastków w: A. porostach, B. sieciach pajęczych (Trzyna et al., 2023).

Porównanie akumulacji na sieciach pajęczych z wynikami z pyłomierza dokonane zostało na innej zasadzie. Jak się okazuje, bezpośrednie porównanie tych dwóch narzędzi jest trudne, stąd w pracy porównawczej skupiono się na porównaniu źródeł pochodzenia cząstek, a nie wartościach liczbowych. Za pomocą analizy głównych składowych (PCA) sprawdzono, czy można zaobserwować jakiekolwiek podobieństwa między wynikami uzyskanymi z zastosowania sieci pajęczych, pyłomierza oraz porostów. Stwierdzono, iż pomimo różnych mechanizmów akumulacji, narzędzia te pozwalają uzyskać bardzo zbliżone wyniki co do głównych źródeł zanieczyszczeń (Rysunek 7). Stąd, jako jedno z głównych źródeł na badanym obszarze wskazano hutę miedzi i/lub zanieczyszczenia transportowe, co zostało również potwierdzone poprzez przeanalizowanie trajektorii wstecznych (HYSPLIT model) oraz zależności pomiędzy zakumulowanymi pierwiastkami.



Rysunek 7 Wyniki analizy PCA dla A. sieci pjęczych, B. porostów i C. monitoringu z wykorzystaniem pyłomierza (Trzyna et al., 2023).

Sieci pajęcze zostały więc ponownie uznane za użyteczne narzędzie biomonitoringowe, które może być wykorzystywane przy ocenie jakości powietrza, szczególnie w badaniach wstępnych, mających na celu wskazanie najbardziej zanieczyszczonych obszarów, tak by później móc przeprowadzić tam bardziej szczegółowy i precyzyjny monitoring.

Wniosek: Analiza ilościowa potwierdza, że akumulacja cząsteczek na sieciach pajęczych jest różna od akumulacji przez porosty. Jednakże oba bioindykatory oraz pyłomierz pokazują zgodne wyniki co do źródeł zanieczyszczeń.

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Comparison of active and passive methods for atmospheric particulate matter collection: From case study to a useful biomonitoring tool

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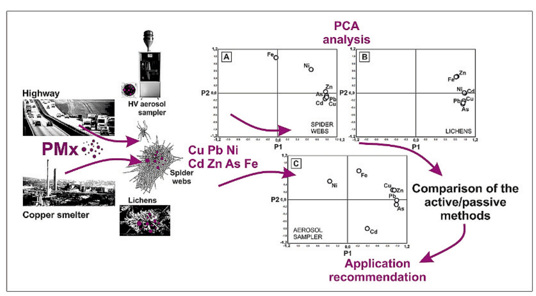
HIGHLIGHTS

- There is a significant difference among the accumulation in lichens and spider webs.
- Bioindicators and aerosol sampler give the same answer in terms of pollution sources.
- It is recommended to use spider webs as a passive sampler for preliminary studies.

GRAPHICAL ABSTRACT



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ABSTRACT

In this study we conducted air pollution monitoring using three different methods: active monitoring with the use of high volume aerosol sampler and biomonitoring with the use of lichens and spider webs. All of these monitoring tools were exposed to air pollution in Legnica city, a region of Cu-smelting in the SW Poland, which is well known for exceeding the environmental guidelines. Quantitative analysis was carried out for the particles collected by the three selected methods and concentrations of seven selected elements (Zn, Pb, Cu, Cd, Ni, As, Fe) were obtained. Concentrations found in lichens and in spider webs were directly compared and indicated significant differences between them, with higher amounts noted for spider webs. Then, in order to recognize the main pollution sources the principal component analysis was conducted and obtained results were compared. It resulted that spider webs and aerosol sampler, despite different mechanisms of accumulation, show similar sources of pollution – in this case – copper smelter. Additionally, the HYSPLIT trajectories and the correlations between metals in the aerosol samples also confirmed that this is the most probable source of pollution. This study can be considered innovative as these three air pollution monitoring methods were compared, which has never been conducted before, and their comparison gave satisfying results.

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1. Introduction

Particulate matter (PM) is known as a mixture of solid and liquid particles suspended in the air (WHO, 2021). PM differs in size, form and chemical composition and can originate from various natural or anthropogenic sources (Seinfeld and Pandis, 2016). In general, smaller PM fractions are considered more dangerous to human health than coarser fractions. This is because small particles, unlike coarse ones, can penetrate deep into human lungs, and they are not easily removed (Hsu et al., 2016). The European Environment Agency (EEA, 2022) states that fine fraction ($PM_{2.5}$) is responsible for about 307,000 premature deaths yearly in the 27 EU Member States, which underlines how severe is the problem with air pollution.

The traditional approach used for the assessment of air pollutant concentrations is based usually on fixed-location monitoring sites, where specific equipment is used for the measurements (WHO, 2021). Providing a high number of these monitoring stations is very important to conduct air monitoring over a large area and define the critical points with a particularly high concentration of hazardous substances. By this the possible range of transport of air pollution can be assessed, which is crucial, as air pollution can also impact the quality of the soil and water (Manisalidis et al., 2020; Soriano et al., 2012).

Even though air pollution is still a growing concern in European countries, the coverage of such monitoring stations is insufficient (WHO, 2021). Moreover, the specific equipment used for such monitoring can have some limitations, i.e. lack of adequate location, the risk of random destruction, the need for access to electricity or the necessity of employment equipment service. These restrictions, as well as high costs, are a big obstacle, and as an alternative, bioindicators could be used.

Some of the most well-known bioindicators are lichens (i.e. Salo et al., 2012; Shukla et al., 2012), which are commonly used thanks to their ability to accumulate different elements in amounts that exceed their physiological needs (Bargagli and Nimis, 2002). These organisms take up nutrients mainly from the air, which is why they are suitable for air pollution biomonitoring. However, there are also many drawbacks, for example, the sensitivity of lichens to various factors such as temperature, humidity or elevation (Lang et al., 1976; Rola, 2020). While lichens are the most active during high humidity episodes, they inhibit photosynthesis in dry periods. Hence, high temperatures negatively influence lichens' processes, but low temperatures in cold seasons also decrease their activity (Armstrong, 1993; Ciężka et al., 2022; Holopainen, 1982; Hyvärinen, 1992).

Other bioindicators that may have fewer drawbacks include spider webs, which have been recently commonly studied as a passive sampler for air pollution monitoring (Bartz et al., 2021; Rybak, 2014; Stojanowska et al., 2022; Trzyna et al., 2022; van Laaten et al., 2020). Spider webs show good properties in collecting PM. This bioindicator has many advantages, i.e. it is cheap, easily accessible and simple to use. What is more, previous studies showed that the transplantation method of the non-contaminated web from laboratory-reared spiders can be successfully applied (Stojanowska et al., 2020, 2021).

Even though the use of spider webs in biomonitoring is getting increasingly popular, it is still not known if the answer they give is consistent with the results from the specific equipment used in the monitoring stations. Such information would answer the question of whether spider webs can be successfully used as bioindicators and whether the response they give is adequate to actual air pollution. Another important study is a comparison of spider webs with another commonly used bioindicator. For now, there are only two studies covering this issue, one comparing spider webs and mosses (van Laaten et al., 2020) and one comparing spider webs and lichens (Stojanowska et al., 2020). Hence, the issue still needs to be focused on.

In this study we conducted air pollution monitoring, using three different methods (two bioindicators and aerosol sampler), and checked if based on the obtained results the same conclusions can be drawn regarding the sources of pollution. Due to many different variables existing between these tools, especially with different units used to express the concentration ($\mu g \cdot g^{-1}$ for bioindicators and $ng \cdot m^{-3}$ for the aerosol sampler) and varying surfaces of the samples (in spider webs and lichens), we concluded that it could be better not to focus on the direct comparison of the concentration of studied elements but rather on the comparison of source apportionment based on principal component analysis (PCA) which allows to focus on searching for common sources of pollution instead of directly comparing the observed concentrations of studied elements. To better identify the main pollution sources the PCA analysis was conducted and the results for spider webs, lichens and $PM_{2.5}$ were compared. Additionally, the HYSPLIT backward trajectories and the correlations between elements in the aerosol samples ($PM_{2.5}$) were studied to support the conclusions regarding sources of pollution. The study was conducted in a heavily polluted area close to a copper smelter in Legnica, Poland. This region is known for exceeding the average annual level of $PM_{2.5}$ given by WHO, and also having high levels of arsenic in PM_{10} (GIOŚ, 2022). The recent annual mean $PM_{2.5}$ concentration in this city was 16.2 $\mu g\ m^{-3}$ in 2020 (GIOŚ, 2021), and in 2021, it was 18 $\mu g\ m^{-3}$ (GIOŚ, 2022). The aerosol sampler was located in the water production plant in Legnica, and in eight different locations, in Legnica city, samples of spider webs and lichens were located. To assess the concentration of the selected potentially toxic elements (PTEs) on the webs, lichens and in the filters the inductively coupled plasma mass spectrometry (ICP-MS) and inductively coupled plasma - optical emission spectrometry (ICP-OS)(for Fe) methods were used, and the obtained results were compared.

To the authors' best knowledge this is the very first study focusing on the comparison of elements collected on the spider webs with the $PM_{2.5}$ collected by the aerosol sampler, and a second study comparing spider webs and lichens. We believe that focusing on this issue is crucial and could enhance the development of the biomonitoring method using spider webs for indication of sources of pollution.

2. Materials and methods

2.1. Study area

Legnica is a city located in southwestern Poland (Lower Silesia voivodship; Fig. 1). The region is characterized by the presence of the Copper Mining and Metallurgical Combine (KGHM), which is one of the biggest copper mining and processing centres in Europe. The KGHM produces mainly electrolytic copper and silver, and gold, lead, palladium, platinum concentrate, and rare earth elements in smaller quantities (https://kghm.com/). The smelter was opened in 1953, and at the beginning it was known for its high emission of fly ash containing PTEs. Even though the emission was significantly reduced compared to previous years (KGHM Cuprum Sp.z.o.o. Research Center, 2007), nowadays there are still some studies indicating the impact of the smelter on the environment (Stojanowska et al., 2020; Strzelec and Niedźwiecka, 2012; Tyszka et al., 2016). Additionally, close to the city, there are also heat and power stations (in Wrocław and Czechnica) and a power station (in Turow; see Fig. 1).

Input in the total production of pollution in this region can be attributed to transport. Nearby, there is the A4 highway (30,000 motor vehicles/day), express national road S3 (about 18,000 motor vehicles/day) and national road number 94 (over 7000 motor vehicles/day) (GDDKiA, 2015). As indicated in the report on the air quality in Legnica, the input of road pollution in the total production of $PM_{2.5}$ in this region is about 13% (Mikołajczyk et al., 2017). The transport pollutants, occurring in the form of PM, arise mainly as a result of tire, brake or road surface abrasion and the rise of pollutants from the road surface (Grigoratos and Martini, 2014). Among the particles originating from the brakes, the presence of Fe, Cu, Zn, Sn, Sb and S can be noted, while among the tire wear particles, there are mostly Zn, Cu and S (Grigoratos and Martini, 2014).

2.2. Methods

2.2.1. Samples collection

2.2.1.1. High volume aerosol sampler. In this study DIGITEL DHA-80 was used as a High Volume Aerosol Sampler for the sampling of $PM_{2.5}$ particulates from the air. The sampler was situated in the area of the Water Production, Water Supply and Sewerage Company in Legnica (51.169 N, 16.133 E), about 2 km southeast from the smelter (Fig. 1). The location of the equipment was dictated by the need to place the equipment in a safe, fenced area with an access to electricity and by the dominating wind directions (Fig. 2). For the samples collection quartz filters (Whatman® QMA) of 150 mm diameter were used. Firstly, before sampling, QMA quartz filters were conditioned in the desiccator, which was done following the PN-EN 12341 norm, and then the weighted filters were directly transported to the $PM_{2.5}$ sampler. The 24 h-samples were collected twice monthly for one year (2 October 2020–24 September 2021) with additional one-week daily aerosol sampling in winter (6–12 February 2021) and one in summer (14–20 August 2021), which gave in total 38 aerosol samples. After the exposition filters were conditioned in the desiccator, which was done following the PN-EN 12341 norm, and then again weighted.

2.2.1.2. Biomonitoring. For this study two spider species, belonging to Agelenidae family, were selected *Eratigena atrica* (C.L. KOCH, 1843) and *Tegenaria agrestis* (Walckenaer, 1802). This family includes 1380 species from 94 genera and has a global distribution (World Spider Catalog, 2023), thus the spiders are easily accessible worldwide. In general, agelenids wave dense sheet like webs, built of irregular thick threads (Rybak and Olejniczak, 2014) which enhance the entrapment of the particulate matter. The spiders from this family do not have the habit of eating their webs (Rybak and Olejniczak, 2014) which allows to obtain the clean, non-contaminated web from the spiders bred in the laboratory conditions. The web produced in the laboratory was stretched on the Petri dishes, which allowed to transplant the bioindicator into the selected study area. The procedure was as presented in the paper by Stojanowska et al. (2021).

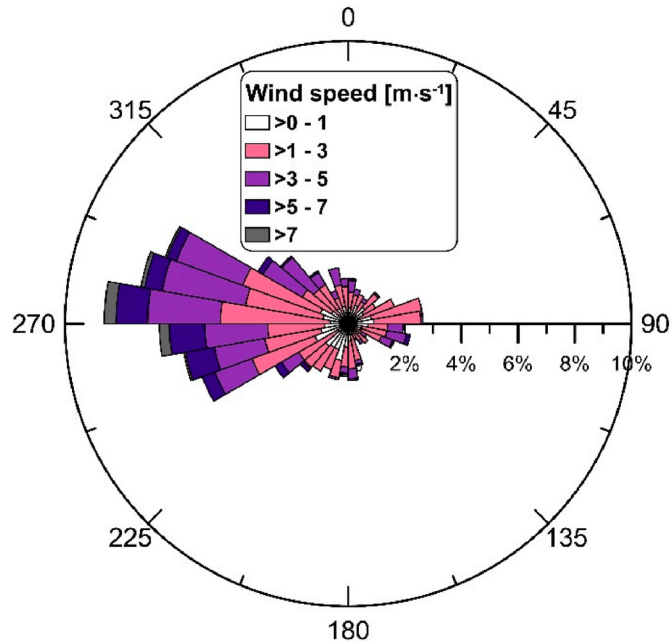

Fig. 2. Wind rose for one-year period (1 October 2020–30 September 2021) of measuring campaign in Legnica.

As a second bioindicator an epiphytic lichen *Hypogymnia physodes* (L.) was used. This species is commonly applied for assessment of the air quality, not only in Poland (Ciężka et al., 2018; Jóźwiak, 2007; Kłos et al., 2018), but in other countries as well (Balabanova et al., 2012; Koroleva and Revunkov, 2017; Poličnik et al., 2004), which indicates its popularity and usefulness. Control lichens were collected from the forest underwood in Stobrawa Landscape Park (Stobrawski Park

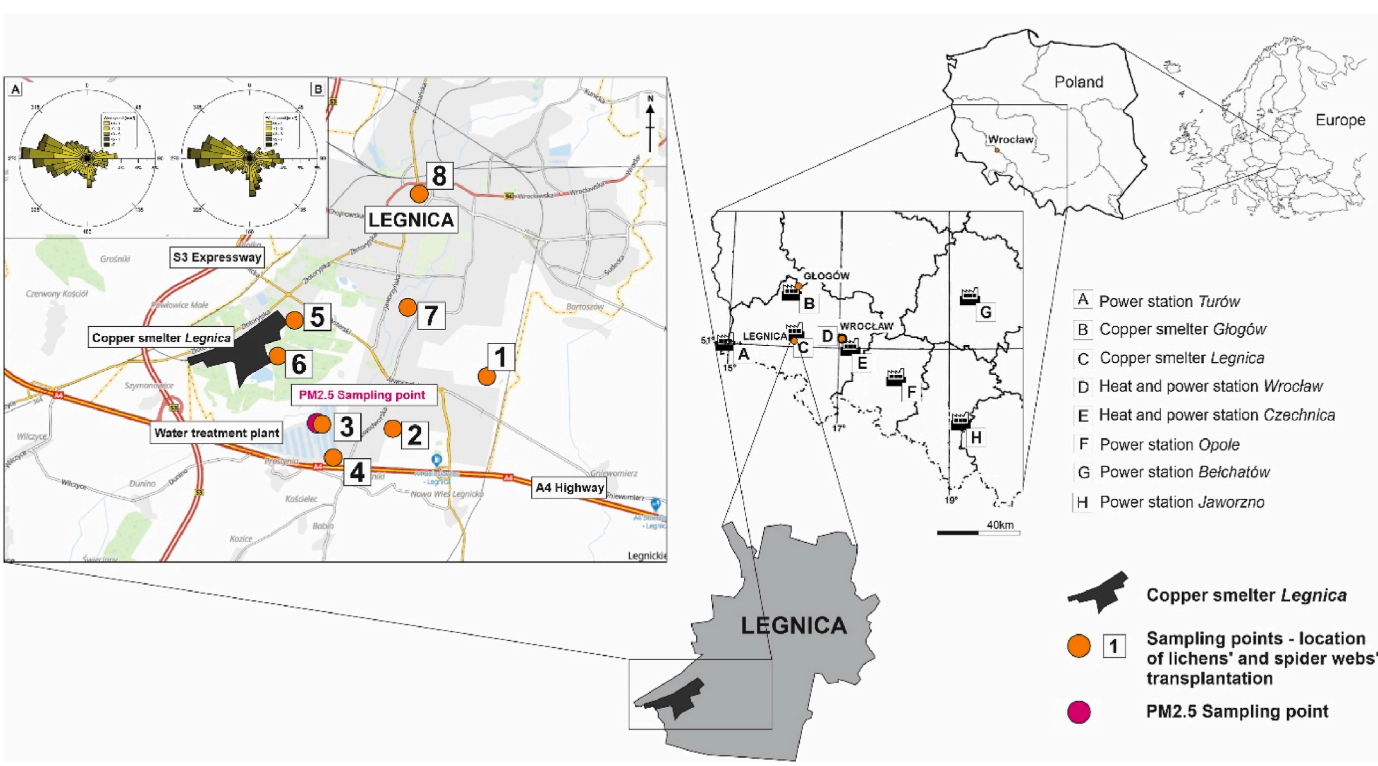

Fig. 1. Location of sampling points in the Legnica region.

Krajobrazowy, 50.882 N 17.871 E), which is supposed to be an uncontaminated region. Collected branches with lichens were tied up together with a line and then transplanted in the study area. In every sampling point one package of about six tree branches of similar sizes was placed.

In the proximity of the smelter a two months sampling (2 August - October 2, 2021) was performed with the use of above mentioned bioindicators (i.e. transplanted spider webs and lichens). The exposure time for both of these bioindicators seems adequate – for lichens relatively short time is recommended (1–3 months) as during longer exposures they might become saturated with studied elements (Bargagli and Mikhailova, 2002). Eight sites were chosen within Legnica area (sampling points 1–8; Fig. 1) and the Petri dishes with the stretched spider web on it, as well as lichens packages, were placed in each sampling point on trees at a height of 1.5 m and left for the exposure. After the selected exposure time, the bioindicators were transported to the laboratory, where the webs were removed from the Petri dishes with sterile glass rod and placed in glass vials while lichens were separated from the branches, dried and packed into clean paper bags. After that the lichens were homogenized with the use of clean fine grit mill made of steel. The next step was weighing the samples three times, using analytical balance Radwag AS 60/C/2 (accuracy 10^{-5} g, temperature 23 ± 2 °C, relative humidity 40 ± 5%). Finally, all of the samples were subjected to the analysis of the content of selected elements.

2.2.2. ICP-MS and ICP-OS analyses

For the inductively coupled plasma - mass spectrometry (ICP-MS) analyses the Elan 6100 DRC-E Perkin (PerkinElmer, Waltham, MA, USA) was used while for inductively coupled plasma - optical emission spectrometry (ICP-OES) Avio 200 (PerkinElmer, Waltham, MA, USA) was used. The concentrations of seven elements (Zn, Pb, Cu, Cd, Ni, As, Fe) were determined in spider webs, lichens, as well as in quartz fiber filters, obtained during monitoring with the use of aerosol sampler. Concentrations of Zn, Pb, Cu, Cd, Ni, As were measured with the use of the ICP-MS method, while for Fe ICP-OS analysis was conducted. At first, webs samples were weighed (approx. 0.03 g each) and weighed quarters of the filters were prepared for analysis. Then they were digested in the microwave reactor (Anton Paar Microwave 3000 Digester, Austria) with the use of the mixture of HNO_3 (Suprapur, 65%, Merck, Darmstadt, Germany) and H_2O_2 (Emsure®, 30%, Merck, Darmstadt, Germany) in the ratio 3:1. The digestion process was as follows: stage 1: power 800 W, time 17 min, stage 2: power 1400 W, time: 35 min. After this the resulting mixture was filtered through the PSE membrane filter (0.22 μm) and then analysed. The following conditions were set: ICP RF power: 1125 W, nebuliser gas flow rate: 0.78–0.83 L·min^{-1}, auxiliary gas flow: 1.15 L·min^{-1}, plasma gas flow: 15 L·min^{-1}, and sample flow rate: 1 mL·min^{-1}. The certified multi-element standard stock solutions of Periodic table mix 1 and Transition metal mix 2 (Fluka) were used as the calibration solutions. For the certified reference materials SRM 1648a and SRM 1643e were taken. The SRM 1648a and SRM 1643e were digested in the same way as other analysed here samples. The certified reference materials were received from the National Institute of Standard and Technology (NIST). The abovementioned analyses were performed by the Central Laboratory of Institute of Environmental Engineering Polish Academy of Sciences in Zabrze. The laboratory operates in accordance with the norm PNEN ISO/IEC 17025.

The following detection limits were established: 0.151 μg·L^{-1} for Zn, 0.134 μg·L^{-1} for Pb, 0.048 μg·L^{-1} for Cu, 0.018 μg·L^{-1} for Cd, 0.017 μg·L^{-1} for Ni, 0.019 μg·L^{-1} for As, and 0.019 μg·L^{-1} for Fe. The analyzes were carried out according to PN-EN 14902: "Atmospheric air quality - Standard method for the determination of Pb, Cd, As and Ni in the PM_{10} fraction of suspended dust".

2.3. Statistical analyses

Firstly, the collected data were described using descriptive statistics (Figs. 3 and 4). Then the Shapiro–Wilk (Shapiro and Wilk, 1965) test was

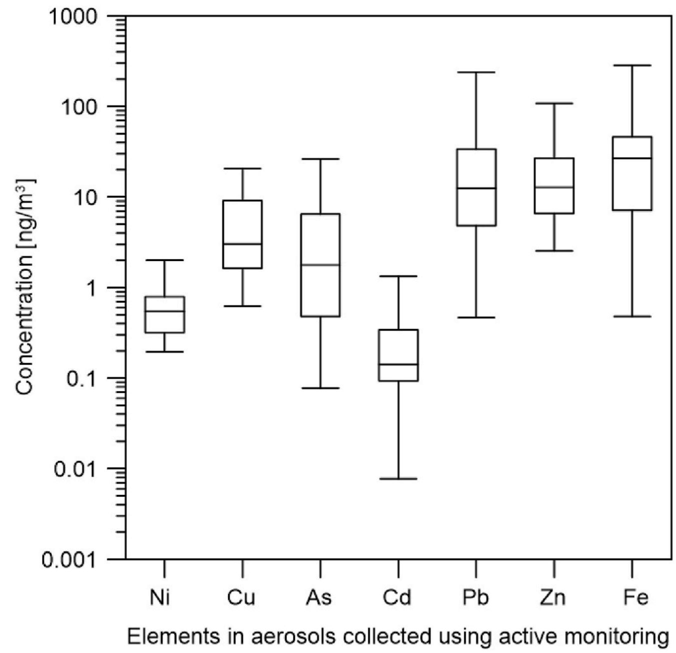

Fig. 3. Concentrations of selected elements collected with the use of aerosol sampler. In the plot, the box represents the interquartile range, whiskers are from the minimum to maximum value, and the median is marked with a line inside the box. Number of analysed samples: 38.

applied with the purpose of deciding whether parametric or non-parametric statistics methods should be used. After that the Mann-Whitney test at $p < 0.05$ was performed to verify the statistical significance of observed differences between lichens and spider webs (Table 1).

Spearman's correlation coefficients were calculated (Sokal and Rohlf, 2012) in order to check the ρ of the relationship between different elements collected by aerosol sampler. This was supposed to confirm the relationships between different elements and by this help in indication of sources of pollution.

Moreover, PCA was implemented here in order to evaluate the parameters controlling the air quality in this selected region (Fig. 5). PCA is a statistical method which is commonly used for identifying patterns in data of high dimension. The STATISTICA® package was applied for PCA performance. It was conducted for spider webs, lichens, and monitoring with an aerosol sampler separately in order to determine the structure of the relationship between element concentrations measured in the webs, in the lichens and in the aerosol collected by the sampler and, based on this, potential sources of pollution were identified. PCA was applied to minimize the set of original variables and to extract a small number of principal components to analyze the relationship among observed variables. It should be underlined that the assumptions of PCA were met (continuity of the variables and the number of elements observed which is greater than the number of original variables). Kaiser criterion was used to leave components that have eigenvalues greater than 1.

Additionally, spatial dependence was checked. It occurs when the studied phenomena in one location increase or decrease the probability of occurrence of these phenomena in neighboring locations. The purpose of studying relations is: (i) information about assigning to objects the values of variables describing the examined features (without taking into account their location), (ii) information about the location of the considered objects - usually as their geographical coordinates. Spatial analysis is an extension of the correlation of variables such as Pearson, taking into account the distances between objects. The distance coding was performed using the Euclidean distance matrix between bioindicator locations. Then, the weighting matrix was determined using the inverse distance method and standardized in rows:

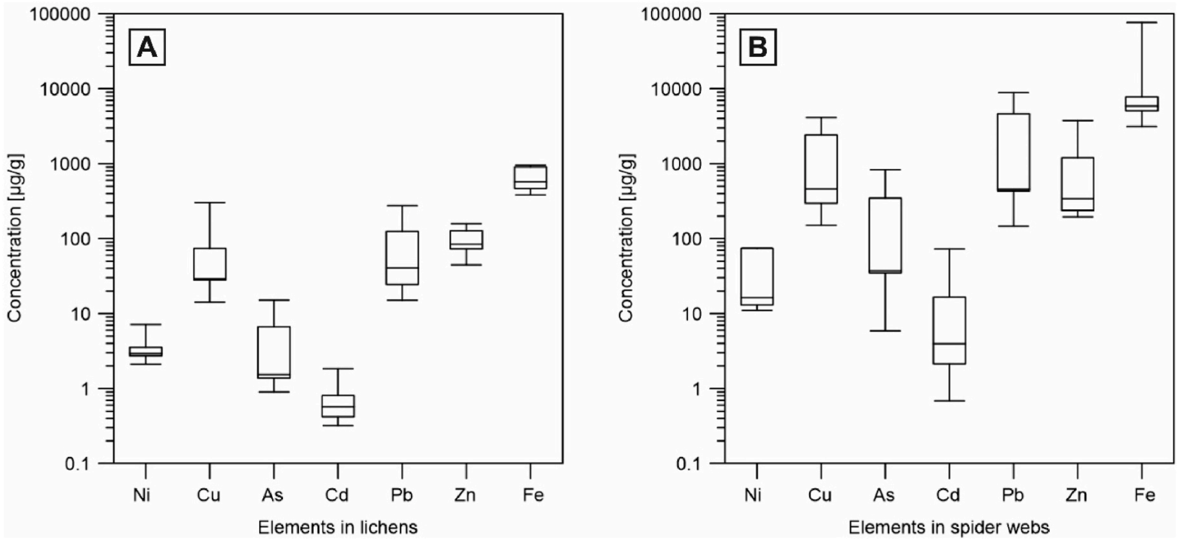

Fig. 4. Concentrations of selected elements in: A. Lichens, B. Spider webs. In the plot, the box represents the interquartile range, whiskers are from the minimum to maximum value, and the median is marked with a line inside the box. Number of analysed samples: 8 for each bioindicator.

Table 1
Results of the Mann-Whitney test ($p < 0.05$) between concentration in lichens and on spider webs.

	Ni	Cu	As	Cd	Pb	Zn	Fe
statistics	−3.78	−3.24	−3.27	−3.11	−3.42	−3.61	−3.78
p-value	0.00015	0.00118	0.00109	0.00187	0.00062	0.00031	0.00016

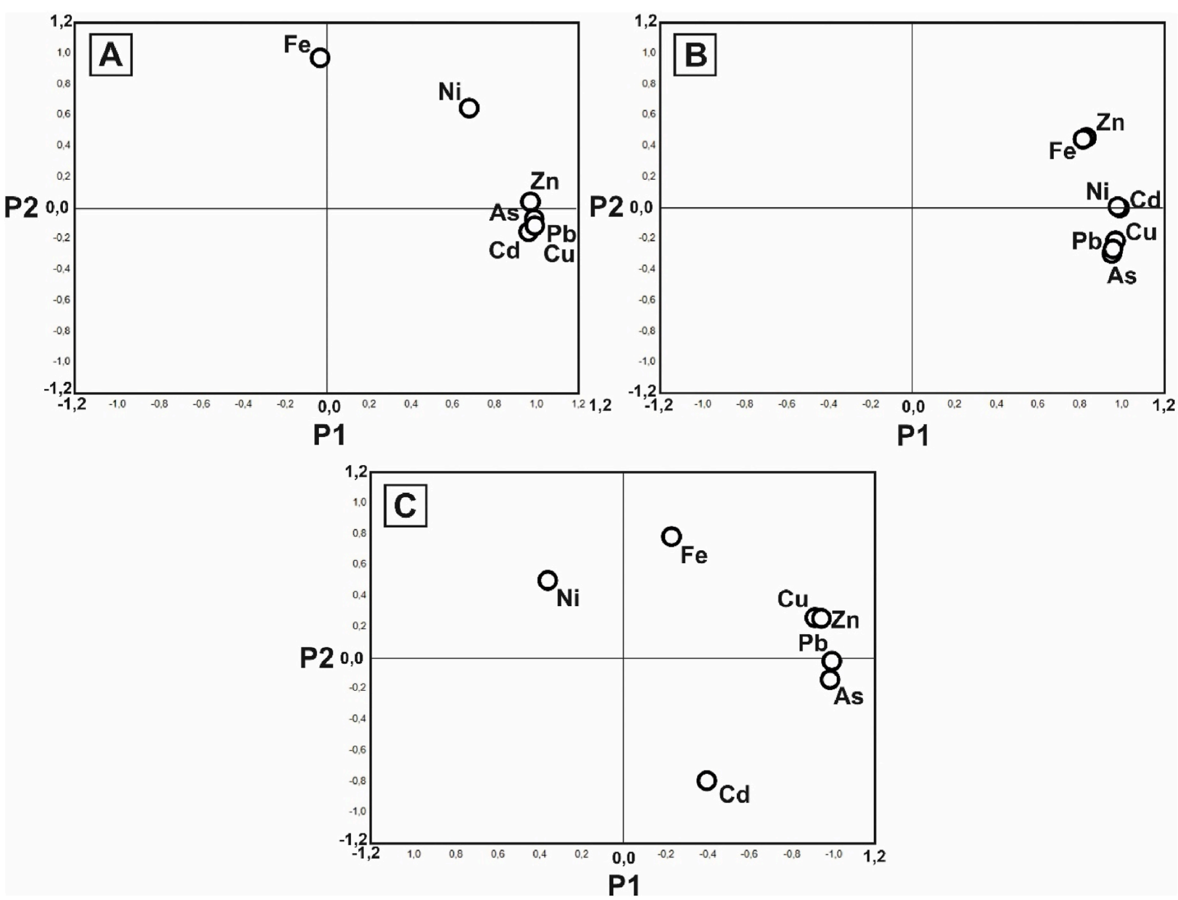

Fig. 5. PCA loadings plot for A. spider webs, B. lichens and C. monitoring with aerosol sampler.

$$w_{ij} = \frac{1}{d_{ij}} \quad w_{ij}^* = \frac{w_{ij}}{\sum_j w_{ij}} \tag{1}$$

where: w_{ij} – element of the weighting matrix, d_{ij} – distance between the object i and j, w_{ij}^* – element of the weighting matrix, standardized with rows.

Moran correlation coefficient (Anselin, 1996) was calculated according to the following equation:

$$I = \frac{\sum_i \sum_j w_{ij}^* (x_i - \overline{x})(x_j - \overline{x})}{\frac{1}{n}\sum_i (x_i - \overline{x})^2} \tag{2}$$

where: x_i – the value of the variable in the location i, $\overline{x}$ – arithmetic mean of the variable X.

The Moran correlation coefficient takes values from the range (−1,1), where a value close to −1 means no spatial dependence (a checkerboard pattern), while a value close to 1 means the separation of space into objects with low values and objects with high values of the variable. Tests of the significance of the correlation coefficients (global and local) were performed using the randomization approach. The expected value and the empirical variance were determined using the permutation distribution of the simulation by the Monte Carlo method (1000 samples). On their basis, a pseudo-p-value was determined to evaluate the statistical significance of the obtained coefficient.

Moran's bivariate local indicators of spatial association (BiLISA) was determined in order to evaluate the relationship between two variables (Anselin, 1996; Kalkhan, 2011). It allows to quantify the relationship between two variables, taking into account the distance between the locations of individual samples (measurements). The coefficient obtained is interpreted analogously to the univariate Moran correlation coefficient described above.

2.4. Environmental parameters

In general, the year 2021 in Poland can be classified as a thermally normal year. The average air temperature in Poland was 8.7 °C, and it was equal to the annual average for many years. In the territory of the

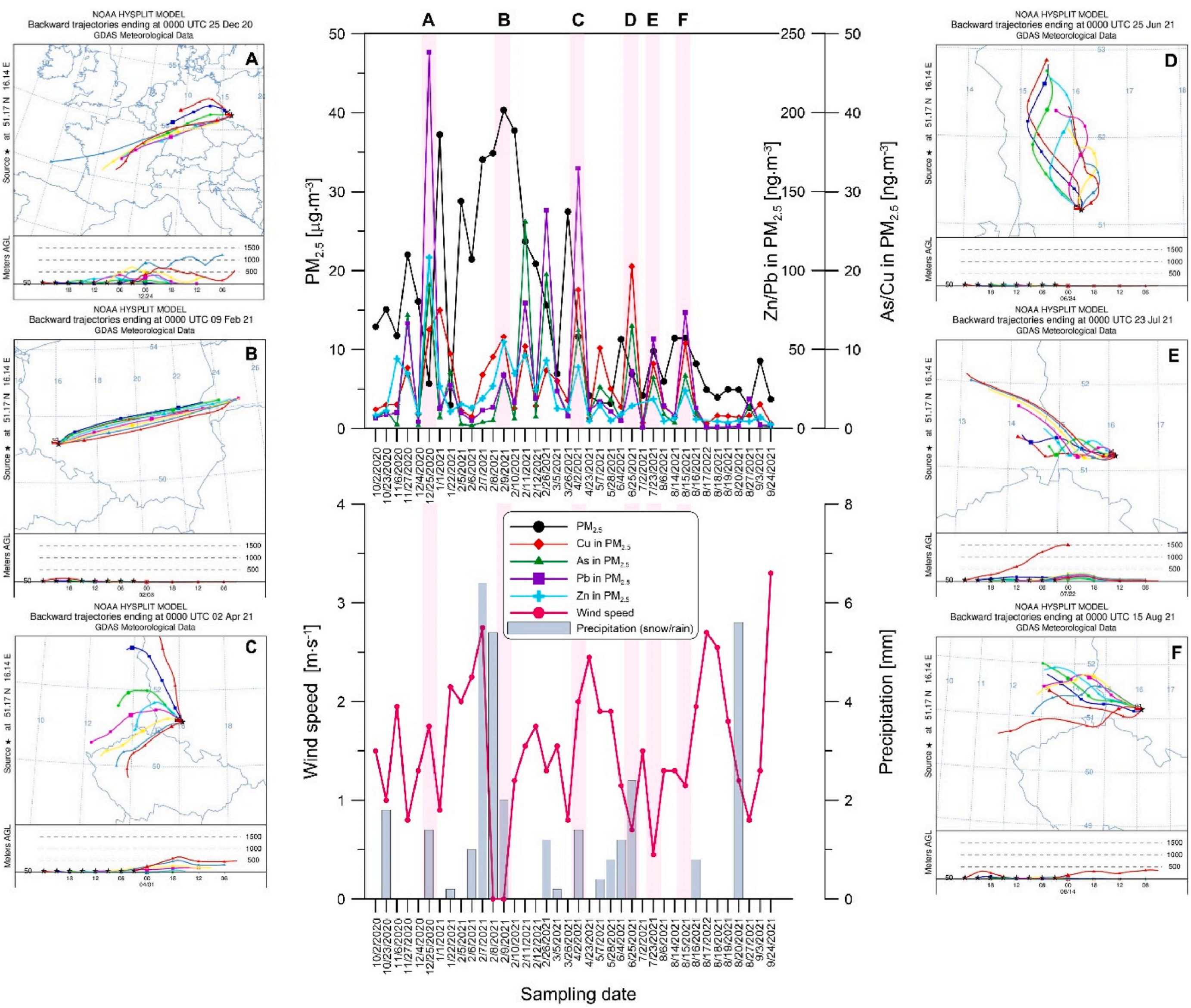

Fig. 6. HYSPLIT 24 h air backward trajectories in LEGNICA calculated for given episodes (A, B, C, D, E, F), concentration of $PM_{2.5}$ and selected elements, and meteorological conditions. For each episode (Fig. 6A–F) eight backward trajectories were calculated every 3 h for the start point 50 m a.g.l and 24 h back to check the height and direction of transported air masses to the PMx sampling point.

Lower Silesian voivodeship the hottest month in 2021 was July, while the coldest moths were January and February. Legnica was one of the warmest cities in the voivodeship with an average annual temperature equal to 9.7 °C. The sum of atmospheric precipitation in 2021 in this voivodeship ranged from 500 mm in the lowland areas of the voivodeship to 1000 mm in mountain regions. Legnica was among the cities with the lowest annual rainfall (442.1 mm; GIOŚ, 2022).

The values for the wind speed for the sampling period (October 1, 2020 to September 30, 2021) for Legnica were obtained by the Institute of Meteorology and Water Management—National Research Institute (IMGW-PIB) synoptic station situated in Legnica (51.193 N, 16.207 E). Based on the obtained data, a wind rose was constructed (Fig. 2) with the use of Grapher 10.0 Golden Software to determine the directions of pollutants transport from potential sources of air pollution.

Additionally, the HYSPLIT model, developed by NOAA (Rolph et al., 2017; Stein et al., 2015), available online: www.arl.noaa.gov/ready/hysplit4.html (accessed on September 27, 2022), was used to track the movement of air masses (Fig. 6). For each sampling period, 24-h airmass backward trajectories were performed at 3 h intervals, at the height of 50 m. The description of the trajectories is presented more precisely in previous publications (Lewandowska et al., 2010; Lewandowska and Falkowska, 2013).

3. Results

3.1. The concentration of selected elements collected by high volume sampler

Air quality monitoring with the use of an aerosol sampler provided the daily (24-h) concentrations of $PM_{2.5}$ on selected days. The minimum daily $PM_{2.5}$ amounted to 2.6 $\mu g \cdot m^{-3}$, while the maximum was equal to 40.3 $\mu g \cdot m^{-3}$, and the average was 14.2 ± 11.2 $\mu g \cdot m^{-3}$. The level of the 24-h $PM_{2.5}$ standard (15 $\mu g \cdot m^{-3}$; WHO, 2021) was notably exceeded during 13 days in the wintertime. The median during the whole sampling period amounted to 11.4 $\mu g \cdot m^{-3}$. The analysis of collected aerosols allowed us to obtain the concentrations of seven elements (Fig. 3).

The analysis of the collected atmospheric aerosols indicated that the most commonly found element was Fe (average 41.7 ± 58.38 $ng \cdot m^{-3}$). Then, in descending order: Pb (30.7 ± 50.09 $ng \cdot m^{-3}$), Zn (20.1 ± 20.73 $ng \cdot m^{-3}$), Cu (5.6 ± 5.07 $ng \cdot m^{-3}$), As (4.4 ± 6.28 $ng \cdot m^{-3}$), Ni (0.7 ± 0.45 $ng \cdot m^{-3}$) and Cd (0.3 ± 0.31 $ng \cdot m^{-3}$) were detected. Analysis of the blank filter sample showed that the amounts of selected elements in the clean filter were negligible. In most cases, the amounts of the elements in the clean filter were below the detection limit, except for Ni, which amounted to 0.16 μg in the whole clean filter, but it was subtracted before the recalculation of the results into $ng \cdot m^{-3}$.

3.2. The concentrations of elements in lichens and spider webs

The concentrations of selected elements (Ni, Cu, As, Cd, Pb, Zn, and Fe) were also checked for both bioindicators (Fig. 4). The preexposure samples of control webs, obtained from laboratory breeding, were analysed in previous research and revealed negligible concentrations of selected elements (Górka et al., 2018). For control lichens, the following amounts of these elements were found in their thalli: 2.1 $\mu g \cdot g^{-1}$ for Ni, 9.9 $\mu g \cdot g^{-1}$ for Cu, 0.4 $\mu g \cdot g^{-1}$ for As, 0.3 $\mu g \cdot g^{-1}$ for Cd, 14.2 $\mu g \cdot g^{-1}$ for Pb, 34.5 $\mu g \cdot g^{-1}$ for Zn and 248 $\mu g \cdot g^{-1}$ for Fe. All of the concentrations were smaller than the results obtained in samples exposed to pollution in Legnica. The samples after exposition showed that in all the cases, the median concentrations for spider webs were much higher than those for lichens (Fig. 4A and B). That trend follows the previous study by Stojanowska et al. (2020), who also showed, that these two bioindicators differed in the accumulated amounts of PTEs.

The only similarity was observed in the case of the order of the most accumulated elements. It was as follows in descending order considering median values: Fe > Cu > Pb > Zn > As > Ni > Cd for spider webs and for lichens it was: Fe > Zn > Pb > Cu > Ni > As > Cd. The most commonly found element was Fe in both cases, but it varied greatly from 3123 $\mu g \cdot g^{-1}$ to 76,465 $\mu g \cdot g^{-1}$ for spider webs and from 383 $\mu g \cdot g^{-1}$ to 954 $\mu g \cdot g^{-1}$ for lichens.

The differences between concentrations in the samples were proven by the Mann-Whitney test ($p < 0.05$), which confirmed that there were significant differences (Table 1), and those differences could be considered large.

3.3. Spatial correlation

The spatial relationships of the identified elements' concentrations in bioindicators at selected measurement points were investigated. First, the global Moran's correlation coefficient (Anselin, 1996) was determined in terms of the concentrations of each element in both spider webs and lichens.

All the coefficients were negative (Table 2), which means a negative spatial correlation, i.e. in the vicinity of locations with observed low concentrations, there are locations with noted high concentrations. The alternating occurrence of low and high values next to each other is clearer for the spider webs. In four out of seven elements (Ni, Cd, Zn, Fe), the coefficient of spatial correlation for the spider webs is further from zero (here smaller) than for lichens. The statistical significance of the coefficients was verified based on the pseudo-p-value determined as the mean of the three-time repeated randomization test with 1000 random permutations. Only for Cd in lichens, Moran's spatial correlation coefficient can be considered statistically significant at the level of $\alpha = 0.1$.

Then, Moran's bivariate local indicators of spatial association (BiLISA) were determined for the concentrations in lichens and spider webs (Table 2). For almost all metals (except Ni), the correlation of point 7 with the adjacent measurement points of the HL type (high value surrounded by low values) is statistically significant at the level of $\alpha = 0.005$. For Fe, the statistics were dominated by the value 76,465.36 $\mu g \cdot g^{-1}$, which was an order of magnitude higher than those recorded in other measurement points.

4. Discussion

The studies on the accumulation of metals in lichens are numerous, and the number of studies using lichen has increased in the last decade (Abas, 2021). The level of accumulation of metals depends on different factors, such as the condition of studied specimens and meteorological parameters, among other factors (Conti and Cecchetti, 2001). Despite this, knowledge of the mechanism of metal absorption in lichens is still not fully understood. Even less is known about the mechanism of metal accumulation in spider webs. It is certainly difficult to directly compare these three techniques used (biomonitoring with spider webs, lichens and active monitoring with the aerosol sampler) because of the different ways of accumulation and deposition of pollutants. Certainly, it is easier to compare webs with lichens, as they are both bioindicators. However, such a comparison has been performed only once (Stojanowska et al., 2020). In this paper, a new attempt has been made to recheck the previously received results. The statistical analysis indicated that the concentrations of elements found in spider webs and lichens cannot be considered similar (Table 1). This is not surprising, as a similar conclusion was also reached in the previous study (Stojanowska et al., 2020), where results of the similarity test showed a clear difference between most of the studied elements. Such differentiation can also be found when comparing spider webs and mosses (van Laaten et al., 2020). The authors also determined significantly higher concentrations of metals for spider webs than for moss bag samples. Such a phenomenon still has no explanation. Probably, the efficiency of entrapment of particles with metals in the case of spider webs is higher than for lichens and mosses. A thick, dense spider web better entraps and accumulates metals, and its protein matrix can bind trapped pollutants, which has been suggested in the case of organic compounds so far (Rybak and

Table 2
Moran's spatial correlation coefficient (pseudo-p-value). Number of analysed samples: 8 for each bioindicator.

	Ni	Cu	As	Cd	Pb	Zn	Fe
Spider web	−0.260 (0.109)	−0.194 (0.308)	−0.214 (0.328)	−0.320 (0.069)	−0.248 (0.231)	−0.292 (0.232)	−0.285 (0.250)
Lichens	−0.165 (0.451)	−0.271 (0.209)	−0.260 (0.172)	−0.242 (0.133)	−0.269 (0.212)	−0.178 (0.475)	−0.078 (0.191)
BiLISA	−0.089	−0.211	−0.238	−0.302	−0.256	−0.303	−0.027

Olejniczak, 2014). Our findings confirm that spider webs are very efficient in terms of PTEs accumulation. Due to that, they could easily replace plant-based methods in all situations when the use of plants is impossible, i.e. due to their limited uptake or unfavourable environmental conditions (drought, cold).

4.1. Spatial distribution

The Moran coefficients were calculated in order to recognize the spatial distribution, and resulted to be negative for all of the studied elements (Table 2). Similar results, but an order of magnitude smaller, were obtained in the study by Gholizadeh et al. (2019), who analysed samples of tree bark in terms of the concentration of Zn, Cu, Pb, and Cd and their possible sources of pollution. All coefficients were statistically insignificant, which means that they do not significantly differ from zero. Negative and at the same time statistically insignificant Moran's coefficients, as obtained in our study, mean random spatial distribution of the feature, i.e. lack of both concentration of results and even distribution in the form of a checkerboard (high values alternate with low ones). Here the result of this spatial distribution might be due to various locations of sampling points, for example, close to roads or close to the smelter. Similarly, in the study of Gholizadeh et al. (2019) the result of spatial correlation was connected to the high variation of metal content among sampling points due to traffic volume and industrial activities. In another study Tepanosyan et al. (2019) used local Moran's I to identify hot spots and spatial clusters of Mo, Pb, and Ti in urban soils of Yerevan. The authors reported that there was a clustering distribution in terms of Pb concentration and built-up urban areas, and spatially correlated with the wind direction. Similar findings, indicating that industrial activity has a high impact on the spatial distribution of metals concentrations were presented by Khosravi et al. (2018).

In our study one surprisingly high result was observed. It was in the case of Fe, for which the highest concentration was noted in the sampling point number 1. This sampling point was located just right next to the railway station (Fig. 1), hence, it can be supposed that the direct location next to the source of Fe pollution can be the main reason of this surprising Fe concentration.

4.2. Principal component analysis (PCA)

The PCA analysis was conducted to check the compatibility of the responses of different methods in terms of indicating the sources of pollution. Results of the PCA indicate that the variability observed in the samples was controlled by two main components. For spider webs (Fig. 5A and SM Table 1), the first two principal components amounted to 95.6% of the total variance. The remaining few percentages constituted a random noise that is not interpretable using this technique (Drever, 1997; Manly, 1998). The first of them (P1) was responsible for explaining 75.3% of the variance. The P1 was loaded highly by Pb, Cu, As, Zn and Cd (0.98, 0.98, 0.99, 0.97 and 0.96). On the other hand, the P2 accounted for 20.3% of the total variance and was loaded highly by Fe (0.97), but also in smaller amounts by Ni (0.65). In general, Cu, As, Cd, Pb, and Zn have very high coefficient for component 1 suggesting its common origin, whereas Ni and Fe have relatively high coefficients for component 2.

For lichens (Fig. 5B and SM Table 2), the first two principal components amounted to 95.3% of the total variance. The rest of the percentages were considered random noise, which is not possible to interpret using this technique (Drever, 1997; Manly, 1998). The first component (P1) explained 86.6% of the variance and it was loaded highly by Ni, Cd, Pb, Cu and As (0.98, 0.99, 0.96, 0.97 and 0.95). The second principal component (P2) accounted for 8.7% of the total variance, and was loaded by Zn and Fe (0.45 and 0.44).

In both of the cases, component 1 (P1) can be connected with Cu, Pb, Zn and As concentrations, hence this component can be attributed to the activity of the smelter because these elements are most commonly found in the emissions from the copper smelting plants (Muszer, 2007; Zhang et al., 2022). Cd can be also attributed to the smelter, as it can be introduced into slag by metallurgical processes (e.g. smelting Zn–Pb ores (Tyszka et al., 2018)). The second component (P2) can be attributed to the linear sources of pollution (i.e. originating from vehicles using local road or from railway pollution), however in the case of lichens it is not so strongly marked. In general, the presence of Fe can be connected with the rail-wheel-brake interactions (Byeon et al., 2015). The railway tracks are located close to the sampling points – just a few km away. On the other hand, Ni's presence can be connected with the local road traffic because the wear of automotive brake pads produces small amounts of this element (Kukutschová et al., 2011). Considering this and the close locations of the commonly used roads (as mentioned in the above subsection about the location characteristics), Ni can be considered traffic-related pollution.

Despite the significant differentiation between the accumulated amounts of the elements in lichens and spider webs, the PCA analysis showed that both biomonitors indicate the same main source of pollution, and this was what was important here. When conducting quantitative biomonitoring studies, it is only possible to know if the amounts of selected elements are higher or lower than those found in other places. However, it is impossible to know if the amount of found PTEs is already negative to human health or not, unlike for specific studies with professional equipment (e.g. high volume aerosol sampler), for which there are given norms, informing about maximum allowed concentrations. In the qualitative terms of biomonitoring, we can connect recorded particles with the possible pollution sources and assess if they give similar answers or not. However, this depends on the monitoring aim and does not apply in general.

Interestingly, the PCA for the $PM_{2.5}$ aerosol samples (Fig. 5C and SM Table 3) shows that we can also distinguish two main components. Component 1 (P1) was responsible for explaining 57.3% of the variance, while component 2 (P2) explained about 23.6% of the variance. It was not possible to extract the third component as the loadings were <0.7 and according to Kaiser criterion also two principal components were recommended. The unexplained variance of almost 20% was a random noise. The first component was highly loaded by Cu, Zn, Pb and As, while P2 was highly loaded by Fe and Cd, but slightly loaded by Ni

Table 3
Spearman's correlation coefficients (ρ) between the data of Legnica samples collected by aerosol sampler [$ng \cdot m^{-3}$]. The significant correlations ($p < 0.05$) are marked by bold font.

	Ni	Cu	As	Cd	Pb	Zn
Cu	0.26					
As	−0.05	**0.76**				
Cd	0.10	**0.71**	**0.80**			
Pb	0.04	**0.78**	**0.92**	**0.84**		
Zn	0.33	**0.72**	0.52	**0.66**	**0.67**	
Fe	0.19	0.16	0.11	0.06	0.04	0.12

(similar to the results for spider webs). Here, on the contrary to spider webs and lichens, Cd is not connected with the first component. Considering the fact that aerosol sampler worked only on the selected days, not continuously, there is a possibility that it recorded the days when the emission of Cd from the slag was slight (Tyszka et al., 2018). Thus, it can be concluded that both results give a similar response in terms of indicating only the main sources of pollution (here: the activity of the smelter). The data revealed that pollution originating from the smelter plays the most significant role in the share of pollution in this region. This stands in accordance with recent studies on particulate matter in this region, which also showed that noted pollution originated mainly from the smelter, and the PTEs especially occurred in the fine fraction (Trzyna et al., 2022). As a second component (P2) influencing this air pollution situation, local road/railway pollution was indicated.

4.3. Identification of sources of the elements - HYSPLIT backward trajectories

Daily variation of the concentration of $PM_{2.5}$, as well as the concentration of specific elements i.e. Zn, Pb, As, and Cu was observed (Fig. 6). This differentiation in the local air quality can be attributed to the influence of the regional sources of pollution or long-range transport. Peaks of the measured values were observed and according to them six episodes (A, B, C, D, E and F) were distinguished. To indicate the potential source of the pollution during each of these episodes, maps of backward trajectories were created (Fig. 6).

In episode A (25 December) the highest concentrations of Pb and Zn were noted among all sampling days, and it was equal to 237.99 $ng \cdot m^{-3}$ and 108.26 $ng \cdot m^{-3}$, respectively. Apart from that, this day was also characterized by one of the highest As concentrations (18.15 $ng \cdot m^{-3}$) during the whole sampling period. Interestingly, the $PM_{2.5}$ concentration was rather low (5.7 $\mu g \cdot m^{-3}$) for this day. According to air mass backward trajectories, this peak of Pb and Zn concentrations can be enhanced by the transport of air mass from the lignite-based power station located on the west of the measuring points (in Poland, Turów). It is known that the process of lignite burning is responsible for the introduction of Pb and Zn into the atmosphere (Czech et al., 2020). The air masses during this day also crossed over the Legnica copper smelter, hence pollution can be brought also from over there. Similar situations were reported in episodes C, E, and F, where very high concentrations of Pb, Cu, and partially As were noted. Considering the dominating wind directions during these days (2 April, 23 July and 15 August), we can see that the pollution is again brought from the west side and by this it can be assumed that it originates from the power station Turów, and partially from local pollutants, i.e. Legnica copper smelter.

Episode B (9 February) represented different meteorological situation and was characterized by the highest $PM_{2.5}$ concentration, equal to 40.3 $\mu g \cdot m^{-3}$. The result is concerning because it significantly exceeds the norm given by WHO (15 $\mu g \cdot m^{-3}$, WHO, 2021). During this day, the second highest Zn concentration was observed (54.79 $ng \cdot m^{-3}$) as well as quite high Cu concentration (11.61 $ng \cdot m^{-3}$). The 9 February date was characterized by almost no wind, which can indicate that the pollution that was noted during this day is rather local than brought from distant places. Hence, the high emissions of Zn and Cu can be attributed to smelting industry in Legnica, which generated metal-bearing pollutants (Muszer, 2007). Moreover, the slight east wind that occurred could bring some pollution from over the city of Legnica, originating, for example, from coal combustion for home heating purposes (Górka et al., 2023).

The highest Cu concentration (20.52 $ng \cdot m^{-3}$) was found on 25 June (Episode D), when also quite a high As value was noted (12.94 $ng \cdot m^{-3}$). The wind during this day came from the north and passed directly through the Legnica copper smelter. Hence, it can be assumed that the observed pollution is directly connected with the processes carried out there. As shown by Dimitrijević et al. (2009), a large portion of anthropogenic As originates from Cu production. Hence, the pollution during this episode can be dominated by Cu smelting processes in Legnica.

To confirm the relationship between different elements in aerosol samples, the correlation coefficients (ρ) were calculated (Table 3). A strong correlation was found between Cu and almost all other elements, except Ni and Fe. This information agrees with the PCA results, which showed that Ni and Fe, unlike other elements, are related to linear sources of pollution (pollution originating from railways/roads). Additionally, the findings seem to be in accordance with the results obtained in the work of Muszer (2007) for another similar Cu smelting region in Poland, where it was shown that the Cu–Ni spherules were the least abundant when analysing the spherules from slag (Muszer, 2007). Similar results were obtained in the research of Bartz et al. (2021), studying PM accumulated on spider webs, where a strong correlation between Cu and Zn, Pb, Cd and As was found, and the Cu–Ni correlation was weak. Our results showed that Ni was not correlated with any of the studied elements, similar to the findings of Bartz et al. (2021). Hence, the origin of the Ni here can be attributed to the road traffic and the wear of the automotive brakes (Kukutschová et al., 2011). Also, a lack of a significant correlation was found in the case of Fe and other elements. This is also not surprising, as Fe was attributed to railway pollution, while almost all the other metals appeared to originate from the Legnica copper smelter. In the case of As, we noted a strong correlation between this element and Pb, Cd and Cu, and a moderate correlation between As and Zn. This finding, together with the fact that a large portion of anthropogenic As originates from Cu production (Dimitrijević et al., 2009), indicates that the impact of the Legnica copper smelter is visible and significant.

5. Conclusions

This study shows that the comparison of element concentrations in lichens and spider webs is possible, in terms of both quantitative and qualitative analysis. The quantitative analysis confirmed that the accumulation of elements in spider web was significantly higher when compared to lichens, which is similar to the previous study and may result from the higher efficiency of entrapment of particles with metals by spider webs in comparison to lichens. Also, the qualitative analysis for both biomonitors stands in accordance in terms of indicating the source of pollution. On the other hand, the quantitative comparison of spider webs with specific equipment (i.e. active monitoring using an aerosol sampler) is quite difficult due to the different units of concentrations of studied elements. In this case, a better option would be the comparison of the sources of pollution (i.e. qualitative comparison) and a main common air pollution source was indicated (copper smelter) in both cases. The possible transport of the pollution from the smelter into the sampling points was also confirmed by the HYSPLIT air backward trajectories, which in most of the studied cases indicated the copper smelter as the main source of pollution, which triggered notable peaks of concentrations.

Despite the difficulty in performing the quantitative comparison for spider webs and the aerosol sampler, this bioindicator proved to be easily used in tracking the sources of air pollution, and in the qualitative assessment of collected aerosols (i.e. regarding the form, size and mineralogical phases of the particles). It is widely known that it would be best to use dedicated aerosol samplers in all cases of air pollution monitoring. However, facing the truth, it needs to be said that it is not always possible. Hence, because of this study, it is recommended to use spiderwebs for screening studies, as they reveal more advantages than lichens and can successfully help in the identification of the sources of pollution. As this is the very first study comparing the particles accumulated on spider web with $PM_{2.5}$ collected by specific equipment, it brings a lot of interesting information and fills the gaps in the current state of knowledge. This research also provides a good foundation for further studies of different mechanisms of accumulation of air pollution in these bioindicators and their possible use in air pollution screening.

Credit author statement

Agnieszka Trzyna: Conceptualization, Formal analysis, Investigation, Methodology, Project administration, Resources, Writing – original draft, Visualization. Justyna Rybak: Conceptualization, Formal analysis, Project administration, Writing – review & editing, Supervision. Maciej Górka: Formal analysis, Writing – review & editing, Visualization, Supervision. Tomasz Olszowski: Resources, Writing – review & editing. Joanna Kamińska: Formal analysis, Data curation, Writing – review & editing. Tomasz Węsierski: Resources, Funding acquisition. Małgorzata Majder-Łopatka: Resources, Funding acquisition.

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Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

Data will be made available on request.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.chemosphere.2023.139004.

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4. Podsumowanie i wnioski

Prowadzone badania udowodniły, że sieci pajęcze mogą dostarczać cennych informacji na temat jakościowego zróżnicowania atmosferycznych cząstek zakumulowanych na ich powierzchni oraz wskazywać, które pierwiastki są deponowane na badanym obszarze.

1) W oparciu o wykonany przegląd literaturowy stwierdzono, że sieci pajęcze mają ogromny potencjał (artykuł 1), jako narzędzie wykorzystywane w biomonitoringu, jednocześnie wskazując na istnienie pewnych luk w aktualnej bazie wiedzy, co stało się początkiem do rozpoczęcia prowadzenia badań w tym temacie.
2) Aby dokładnie rozpoznać źródła zanieczyszczeń na badanym obszarze przeprowadzona została złożona analiza jakości powietrza, która wskazała na sezonową zmienność zanieczyszczeń atmosferycznych. W okresie zimowym zaobserwowano znaczny wpływ niekompletnego spalania paliw kopalnych, natomiast latem, dominujący był wpływ cząsteczek biogenicznych oraz transportu drogowego (artykuł 2).
3) W celu sprawdzenia, czy sieci pajęcze mogą być równie użyteczne, tak jak i inne powszechnie znane i wykorzystywane bioindykatory, przeprowadzona została analiza porównawcza metod. Prace nad tematem badawczym dostarczyły informacji, że w porównaniu do porostów sieci pajęcze kumulują dużo większe ilości pierwiastków potencjalnie toksycznych (artykuł 3 i 8).
4) Ilościowe porównanie akumulacji pierwiastków na sieciach pajęczych (bioindykator pasywny) z akumulacją pierwiastków na filtrach przez analizator automatyczny (pyłomierz) dla tego samego okresu czasu wykazało rozbieżności w uzyskanych wynikach (artykuł 4). Sieci pajęcze akumulują większe ilości cząsteczek zanieczyszczeń, co powiązane zostało z selektywnym pobieraniem frakcji przez pyłomierz (głowica PM_{10}), który wyklucza pobór agregatów i cząstek większych niż PM_{10}.
5) Jakościowa charakterystyka cząsteczek zanieczyszczeń powietrza, przeprowadzona z wykorzystaniem SEM-EDX, udowodniła iż grubsze frakcje zlokalizowane są na sieciach w stosunkowo niewielkiej ilości i są one raczej mało zróżnicowane pod kątem faz mineralogicznych, a przeważającą część stanowią wśród nich cząsteczki pochodzenia naturalnego. Drobniejsza frakcja wykazała większe zróżnicowanie mineralogiczne (dominowały cząstki antropogeniczne) i występowała zdecydowanie

liczniej (artykuł 5 i 6). Analiza porównawcza wyników obu metod tj. SEM-EDX i ICP-MS dostarczyła satysfakcjonujących wyników pod względem środowiskowym.

6) Dane ilościowe, określające zawartość pierwiastków zakumulowanych na sieciach pajęczych, mogą z powodzeniem posłużyć do obliczenia narażenia zdrowotnego (artykuł 6 i 7), a dzięki temu możliwe jest oszacowanie realnego wpływu zanieczyszczeń powietrza na zdrowie człowieka na danym obszarze.
7) Wartościowe okazało się porównanie źródeł pochodzenia cząstek, które wskazało na zgodność odpowiedzi dla trzech analizowanych metod: biomonitoring z wykorzystaniem sieci pajęczych i porostów oraz metoda aktywna (artykuł 8).

Podsumowując przedstawione wnioski z wymienionych prac (artykuły 1-8), sieci pajęcze mogą z powodzeniem wspomagać proces określania pochodzenia cząstek zanieczyszczeń powietrza, a na podstawie ilościowej zawartości wybranych pierwiastków w pyle zakumulowanym na sieciach możliwe jest także oszacowanie ryzyka zdrowotnego. Niezwykle ważny jest też fakt, że informacja na temat źródeł pochodzenia aerozoli atmosferycznych, uzyskana poprzez analizy sieci pajęczych, jest zgodna z informacją otrzymaną z metody referencyjnej. Wykorzystanie tak taniego i łatwo dostępnego bioindykatora może znacznie zminimalizować koszt przeprowadzanych badań monitoringowych, prowadząc do łatwego zwiększenia ilości punktów pomiarowych. Pomimo tego, że sieci pajęcze na chwilę obecną nie zastąpią metod aktywnych (pyłomierze, analizatory etc.), to mogą być one bardzo dobrym narzędziem do przeprowadzania wstępnych badań oraz uzupełniania stosowanych obecnie metod referencyjnych. W celu uzyskania szczegółowych informacji o jakości powietrza na badanym obszarze zaleca się jednak stosowanie wielu różnych metod/analiz jakości powietrza, które minimalizują ryzyko wyciągnięcia błędnych wniosków.

5. Pozostały dorobek naukowy

1) *Ocena jakości wody (gmina Złoty Stok, Dolny Śląsk) zanieczyszczonej arsenem w oparciu o makrozoobentos.* Magda Szmigielska, Magdalena Wróbel, **Agnieszka Stojanowska**, Justyna Rybak. *Inżynieria Ekologiczna*. 2018, vol. 19, nr 4, s. 58-63.
Punktacja MNiSW: 9

2) *Analysis of the vegetation in the terrain of closed industrial waste dump in Siechnice (Lower Silesia).* Łukasz Winkler, **Agnieszka Stojanowska**, Justyna Rybak. *Journal of Ecological Engineering*. 2019, vol. 20, nr 5, s. 242-248.
Punktacja MNiSW: 70

3) *The impact of chemical contaminants on biocenosis (ecotoxicological studies).* Magdalena Wróbel, **Agnieszka Stojanowska**, Martyna Nosarzewska, Radosław Rutkowski, Justyna Rybak. EDP Sciences. 2019, art. 00088, s. 1-7. (E3S Web of Conferences, ISSN 22671242; vol. 100).
Punktacja MNiSW: 15

4) *Assessment of the "Oława" smelter (Oława, Southwest Poland) on the environment with ecotoxicological tests.* Klaudia Radlińska, Magdalena Wróbel, **Agnieszka Stojanowska,** Justyna Rybak. *Journal of Ecological Engineering*. 2020, vol. 21, nr 3, s. 186-161.
Punktacja MNiSW: 70

5) *Environmental health hazards of the demolition of the 'Siechnice' smelter slag heap.* Paulina Łukasik, Magdalena Wróbel, **Agnieszka Stojanowska**, Farhad Zeynalli, Justyna Rybak. *Ecological Engineering & Environmental Technology*. 2021, vol. 22, nr 4, s. 74-85.
Punktacja MNiSW: 20

6) *Can Abies alba needles be used as bio-passive samplers to assess air quality?* **Agnieszka Stojanowska**, Maciej Górka, Anita Urszula Lewandowska, Kinga Wiśniewska, Magdalena Modelska, David Widory. *Aerosol and Air Quality Research*. 2021, vol. 21, nr 11, art. 210097, s. 1-23.
IF: 4.530
Punktacja MNiSW: 100 pkt

7) *The comprehensive health risk assessment of Polish smelters with ecotoxicological studies.* Magdalena Wróbel, **Agnieszka Trzyna**, Farhad Zeynalli, Justyna Rybak. *International Journal of Environmental Research and Public Health*. 2022, vol. 19, nr 19, art. 12634, s. 1-16.
IF: 4.614
Punktacja MNiSW: 140 pkt

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