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PRELIMINARY ASSESSMENT OF USE OF SPIDER WEBS FOR THE INDICATION OF AIR CONTAMINANTS

Spider webs found in polluted areas could absorb air contaminants. In order to check their cumulative ability, two different study sites had been chosen in Wrocław (in the area of wet ponds and in the residential district of Biskupin) where spider silk was collected (after 10 days from the time of its construction). Web types of appropriate thickness and size were chosen for analyses. The representatives of Agelenidae family belonging to two species *Malthonica silvestris* and *Malthonica ferruginea* proved to be the most adequate for further studies. The level of selected heavy metal cumulation was assessed (Pb, Zn, Pt) in the collected samples. As the background, the level of air pollution concerning dust and selected heavy metals was also analysed by classic methods. Based on the web analysis, it was found that site 2 (Biskupin) exhibited the highest level of pollution with some metals. Similar results were obtained with the application of classic methods. The results of research are promising and confirm the possibility of obtaining a practical tool for the indication of air pollutants based on spiders silk, particularly on webs belonging to Agelenidae family.

1. INTRODUCTION

Combustion gases are much more harmful to people than pollutants deriving from the industry, because they spread in higher concentrations, on lower heights in the direct vicinity of people [1–3]. Air pollution causes annually about 6% of all recorded fatal cases [4]. The pollution coming from transport is responsible for half of them. The research conducted in tunnels, multi-storey car parks, under the bridges and in surroundings of petrol stations showed from 4 to 40 times higher concentration of pollutants than in the entire urban areas. It was estimated that 15 mln of hectares of Poland, almost half of the territory of our country, remains directly under the influence of emission coming from the motorization [3, 5]. In the city, the total concentration of carcinogens in air is about fivefold higher than outside the city [6]. The engine combustion gases contain a lot of carcinogens causing, in a long-term exposition, devel-

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opment of cancer cells. The most dangerous are benzene, polycyclic aromatic hydrocarbons (PAH), dust and heavy metals. Dust is a serious threat. Coal particles have very high absorption capacity and therefore diverse toxic substances settle easily on their surface, including carcinogenic hydrocarbons and heavy metals [7]. Dust participates in transporting them inside the human body. It irritates eyes, skin and respiratory tract (pneumoconiosis). Diesel engines are main source of dust emission [8].

As spider webs absorb air pollution from the environment, they can be useful indicators of air quality. The advantages of application of spider webs are as follows: low cost of samples collection, availability of the research material, secluded location preventing their destruction by weather conditions (falls, wind, snow) and people, non-invasiveness of studies (no need of killing animals), easy collection of samples. Moreover, studies conducted so far [9] show that cumulative ability of webs is an additional advantage. Such ability, being a consequence of its chemical structure, gives an unique opportunity to asses an air pollution level in a long-term period, contrary to the classic measurements which could only deliver information about the temporary state of the environment. Additionally, measurement of concentrations of pollutants is usually carried out with expensive and inconvenient equipment (large-sized and noisy apparatus). On the opposite, webs collection from tunnel walls is fast and enables one to study a long-term influence of pollutants only by single examinations (e.g. 7 or 30 days).

Application of high-tech passive dosimeters formally discredits the legitimacy of webs use, however it is worth to emphasize that even a relatively cheap and simple dosimeters cannot be left in random places in case of theft or destroy. Another advantage is that webs are usually found in large numbers, often in places where it is hard to install the dosimeter and usually do not attract any attention. What is more, it is possible to date the time of the web exhibition to pollutants by removing the old web and using only a new construction.

Cumulative ability of spider webs has not been analysed in Poland. Assessment of usefulness of webs for the indication of the environment is the aim of presented studies. The obtained results could contribute to the development of an easy method of pollution indication which can function almost all year round (webs can be obtained under laboratory conditions by breeding spiders) which could be an additional advantage of the method, unlike the majority of bioindication methods where application is often limited only to the vegetative season (e.g. assessment of water quality based on benthic macroinvertebrates) [10, 11].

2. EXPERIMENTAL

Webs were collected from the two following study sites within city of Wrocław.

Site 1. Hydrotechnical building on water supplying areas of Wrocław (wet ponds) is located in the south-east part of the city. A flat area (1026 hectares) consisted of meadows, only partly overgrown with bush and trees, covered with the system of ditches and channels supplying water to 63 infiltration ponds. Drinking water is delivered for the city of Wrocław from this area and from the river Oława, which is fed with water from Nysa Kłodzka. The area lies distantly from the main communications trails. Spider silk was collected from the hydrotechnical building.

Site 2. Biskupin, the housing estate which is situated in the eastern part of Wrocław, in Śródmieście district. Odra River constitutes its natural south border. Surroundings are diversified including areas of allotments, parks, high buildings (post-war tenements) and low buildings (detached houses). Spider silk was collected from fences and walls separating premises of Kosiby street.

Webs of two species: *Malthonica silvestris* (site 1) and *Malthonica ferruginea* (site 2) have been analysed, both belonging to Agalenidae family. *Malthonica silvestris* constructs triangular webs lengthening to the funnel where the spider stays all day long (retreat). This species inhabits forests, places under stones, roots and blown down trees. Moreover, it is possible to find *M. silvestris* in ruins, tunnels, as well as in caves [12]. *Malthonica ferruginea* (with rust-coloured abdomen lives in forests or in surroundings of human residences. Both species belong to the same family, weave the similar structure (web of similar density), thus it was possible to compare the cumulative ability of this construction in both sites.

Agelenidae family prefers dark, derelict and neglected buildings, its representatives can also be found in tunnels and under bridges. Webs are not sticky (as webs of many representatives of Ecribellatae suborder), consist of an opened residential tube which widens at the front into the funnel but its lower part changes into an extensive silk carpet with numerous signal threads, informing the spider of preys passing by. Flies and other insects are the main prey of Agelenidae [12].

In order to check whether spider webs are able to indicate the pollution level exceeding background values, concentrations of selected metals were defined and compared only among webs of newly constructed and then collected in both study sites. The dependence of webs distance from the source of emission and the influence of webs age on the level of cumulation is the crucial matter which has already been proved in previous studies [9]. These findings were taken into consideration in presented analyses.

Webs of both species were collected from April to the end of May in 2009. Only new constructions were taken into consideration. For that purpose, the area of studies was marked and photographed in detail and all old constructions were removed. Once a day sites were controlled in order to notify the appearance of the new webs. New constructions were collected after each 10 days.

After the defined time the silk was gathered into clean glass phials with glass, sterile baguettes, then webs were frozen for the future chemical analyses (the method after Hose et al. [13]). For mineralization purpose, the samples were defrosted, dried by

48 h at 70 °C and weighed with the accuracy of 0.0001 mg, digested in nitric acid (70%) and warmed for drying off. Samples were suspended again in nitric acid, and then hydrogen peroxide was added (30%). Remains were again suspended in nitric acid and warmed to 120 ° to total digesting. Next, samples were analysed for the Pb, Zn and Pt presence. Elements chosen for analyses are pollutants most toxic for humans.

ICP-MS, ICP-OES and AAS analyses were made in a Chemical Laboratory of Multi-Elemental Analyses, Institute of Inorganic Technology and Mineral Fertilizers in the Chemical Department of Wrocław University of Technology. The analytical scheme applied at the laboratory gives the possibility of performing multi-elemental analyses. A low detection limit enables determining concentrations of elements of ultratrace level (with the application of the most sensitive technique ICP-MS), microelements (ICP-OES with an ultrasonic nebuliser) and macroelements (ICP-OES with a pneumatic nebuliser). Determining of a wide range of concentrations, with the use of all sorts of ICP apparatuses enables a precise analysis of a delicate material such as spider silk (the sensitivity for Pt and Pb was 0.2 ppm and for Zn 0.01 ppm).

As a background, the level of air pollution with dust PM2.5 (dust particles smaller than 2.5 μm) was analysed on both sites by classic methods. The samples collection performed in the period of March–May of 2009 contained twenty-four hour samples of PM2.5 dust) within the area representing the municipal background (site 1) and urban area (site 2). Twenty-four hour PM2.5 samples were taken with the impactor which has been applied in the United States for a dozen years in the program of Interagency Monitoring of Protected Visual Environment IMPROVE [14]. Dust was collected on Teflon filters (Whatman, 2 μm PTFE 46.2 mm, air flow 22.8 dm^3/min). Analyses of chemical composition were performed with the fluorescence technique, of X-ray XRF, PIXE (induced X-Ray energy proton) and PESA (proton elastic scattering analysis) in PANalytical (Almelo, the Netherlands). The details of sampling and the accuracy of analytical methods have been presented by Horemans et al. [15]. PESA is usually applied in studies of hydrogen concentrations in samples. Concentrations of 22 elements have been analysed (H, S, Cl, K, Ca, Ti, Fe, Mn, Cr, V, Ni,Cu, Zn, As, Pb, Sr, Br, Rb, Sr, Na, Al, I i Si). All data were analysed with t- test (critical value 0.05).

3. RESULTS

Both sites were significantly different ($P < 0.05$) concerning the concentration of Pb, Zn and Pt in new constructions of *M. silvestris* and *M. ferruginea*. Table 1 shows average concentrations of metals cumulated in webs for both species of spiders in two studied areas. Figure 1 shows average concentrations of elements recorded within the area of municipal background (site 1) and in the city centre of Wrocław (site 2). Average twenty-four hour Pb and Zn concentrations differed significantly ($P < 0.05$). Higher concentrations were generally observed in the municipal atmosphere.

Table 1

Average concentrations of metals (± standard deviation) in newly constructed webs of *M. silvestris* and *M. ferruginea* (sites 1 and 2)

Species	Site 1	Site
M. silvestris		
Pb	45±6 μg/g	–
Zn	201±26 μg/g	–
Pt	27±5 ng/g	–
M. ferruginea		
Pb	–	85 ±4 μg/g
Zn	–	317±12 μg/g
Pt	–	67±23 ng/g

4. DISCUSSION

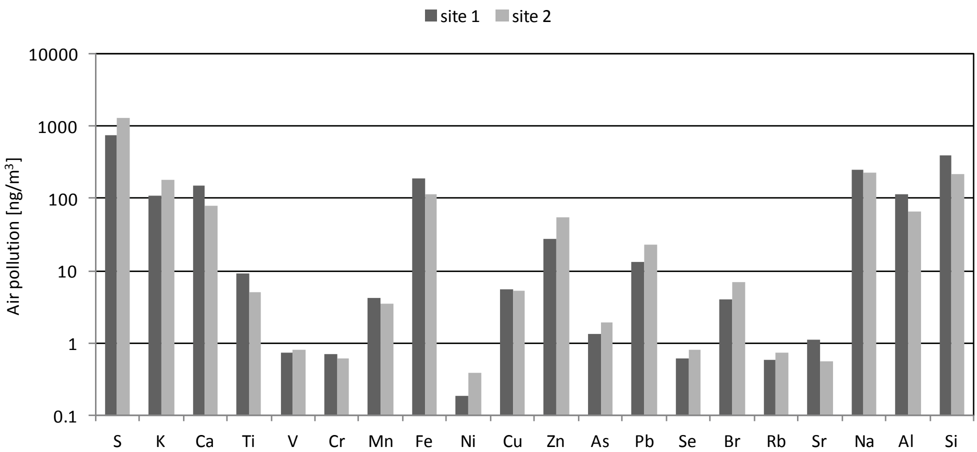

Fig. 1. Average concentrations of elements recorded within the area of the municipal background (site 1) and in the city centre of Wrocław (site 2)

The obtained results show a relatively high level of metals content in both sites. Site 1, as web analysis shows, was characterised by a relatively high concentration of Zn (water-supplying areas) compared with studies conducted by Hose et al. [13]. Such high values are surprising; they could be result of limited, but still present car traffic in this area or in general the high concentration of Zn in the municipal background. Nowadays, brake pads are primary source of lead [16]. Engine oil, tyres usage are the basic source of pollution with zinc [17]. However, it can also originate from corrode of building materials [18]. Differences in Zn, Pb and Pt content in webs compared with the results achieved by Hose et al. [13] could also be connected with the age of studied webs. A choice of spider species for studies could be also important factor influencing results (Hose et al. [13] examined webs of species which are not recorded in Poland), thus such comparison could only give rough values.

The emission deriving from transport decreased significantly since the introduction of lead-free petrol, however application of catalytic converters causes the emission of other harmful metal – platinum. Platinum is teratogenic (by damaging the foetus), is excreted with urine leading to kidneys injuries. Small amounts of platinum compounds are also strong allergens [3]. However, concentrations recorded in our studies are surprisingly high, posing a great threat to people and environment. The content of this element in spider silk has never been analysed, therefore it is not possible to make any comparison. However, it is possible to compare the results of the study with the concentrations recordec in dust collected in the vicinity of busy streets of Beijing. The obtained values were from 3.96 to 356.3 ng/g, however referential sites cumulated from 0.1 to 0.9 ng/g of Pt [18]. In our studies, site 2 achieved the highest value (67 ng/g), site 1 was characterised by much lower value (27 ng/g) but not as low as got referential site in Beijing.

Analyses performed with the use of classic methods show that site 2 is generally characterised by higher level of air pollution (Fig. 1) and achieved values for Pb 23 ng/m^3 and Zn 54 ng/m^3. However, in the area of municipal background (site 1) contents of Pb were 13 ng/m^3 and Zn 27 ng/m^3. When we compare the recorded concentrations of Pb and Zn in Wroclaw with literature data it can be concluded that they fall within the range which was obtained in the world. Average concentration of Zn in the atmosphere of urban agglomeration of Cincinnati, USA, obtained from a few measuring sessions, was 10–211 ng/m^3 depending on the season and location of measuring stations [19]. The highest values were recorded in the period from August to September in the city centre. Pb concentrations were much lower, from 3 to 28 ng/m^3. In Vienna (Austria) annual average values, in the municipal area, were Zn for and Pb from 22 to 17 of ng/m^3, however in the area located 30 km away from the city the values were lower, appropriately 17 and 12 ng/m^3 [20]. Next, in the fast developing cities of Asia concentrations of Zn and Pb were 245 and 79 ng/m^3 [21]. Nevertheless, it should be taken into account that annual values are always averaged from measurements conducted within a year and are usually lower than these recorded at short periods of time.

5. CONCLUSIONS

The aim of our studies was a preliminary assessment of the possibilities of use of spider webs for the indication of main air pollutants. The results of the study are promising and confirm the working thesis that webs can serve as an effective tool for the indication of pollutants. Webs of two Agelenidae representatives used in ours research should be taken into account particularly because of their very good cumulative properties deriving from high density.

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