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Research Article

Heavy Metals Assessment in Urban Air of National Capital Region of Delhi Using Spider Webs as Bioindicator

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Abstract

Background and Objective: Delhi represents one of the most polluted cities of the world where the levels of air pollution are alarming. The present study aimed to investigate the efficiency of spider webs as bioindicator of heavy metal pollution in urban air of National Capital Region (NCR) of Delhi. **Materials and Methods:** The webs of *Cyrtophora citricola* (*C. citricola*) (Forskål, 1775) were used that were collected from road side areas at five different sites of NCR region. One laboratory spider web was spun to use as a control sample. The webs were digested with concentrated HNO_3. Metal concentrations were analyzed by flame Atomic Absorption Spectrophotometer (AAS) to determine the accumulation ($\mu g\ g^{-1}$) of selected heavy metals (Pb, Zn, Ni, Cd, Cu and Cr) in the webs. **Results:** The highest concentration of all heavy metals except Cr was recorded in the webs collected from two industrial sites. Also, the mean concentration of all heavy metals except Cr was found to be higher at industrial sites in comparison to residential sites. In the overall area, mean concentration of Zn was found to be highest followed by Pb, Cr, Ni, Cu and Cd. **Conclusion:** Findings of this study confirm that webs of *C. citricola* can be used as a bioindicator of heavy metal pollution in air of NCR Delhi and demands for testing the webs of other common spiders of this region for this purpose.

Key words: Heavy metals, urban air, spider web, bioindicator, *Cyrtophora citricola*

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Competing Interest: The authors have declared that no competing interest exists.

Data Availability: All relevant data are within the paper and its supporting information files.

INTRODUCTION

Spiders (Phylum: Arthropoda, Class: Arachnida, Order: Araneae) constitute one of the most heterogeneous faunal groups after insects, represented by a total of 47,304 species belonging to 4076 genera and 116 families worldwide[1]. Of these, 1868 species and 479 genera in 64 families are reported from India and 51 species belonging to 41 genera and 15 families are reported from Delhi[1,2].

Spider web is one of the precious gifts of nature and the evolution of spider silk with spider speciation in the evolutionary history of spiders is fascinating. Spider silk is the key to the success of this group on the earth and spiders have also evolved efficient ways by consuming and recycling their own web silk[3]. Spider silk has lots of applications in human use. Some spider silk possesses high tensile strength and are used to produce bullet-proof jackets, bandages and surgical threads and potential source of artificial tendons and ligaments[4-6]. It contains antimicrobial properties[7,8] and silk fibroin protein is proved to be anti-diabetic in type 2 diabetic persons[9]. Web silk can arrest the airborne particles[10-21] and also trap pollens[22]. Thus, though spider webs are commonly available, it is a valuable bioresource in urban extent. Being the national capital of India, Delhi is not an exception.

Delhi has a city forest and the Delhi ridge lies near the bank of river Yamuna. It is passed over by one of the oldest mountain systems of the world, the Aravalli hills and the city represents the third most populated city in India[23,24]. It is the vehicular pollution, which comes as the major problem for the city, which has the highest number of automobiles in the country[23,24]. It is one of the most polluted cities of the world[23-26]. According to the white paper on the pollution prepared by the Ministry of Environment, Forest and Climate Change, Government of India, the ambient air quality data of Delhi shows very high values of suspended particles which have been found beyond the permissible limits from last several years continuously[26].

Keeping in mind spider webs as inexpensive and readily available biomaterial and useful to assess air quality monitoring for heavy metals[10-21], the present study was undertaken to find out effectiveness of spider webs as a bioindicator to investigate heavy metal pollution levels in Delhi NCR, where vehicular pollution is the major problem and particulate matters and other aerosol particles in air are beyond the prescribed limits[23-26]. For this study, a single species viz. *C. citricola* (Forskål, 1775) was selected which is commonly found in all types of habitats in Delhi NCR. The purpose of this study was to determine the concentration of heavy metals like Pb, Zn, Ni, Cd, Cu and Cr trapped in webs of *C. citricola* from selected industrial and residential sites of Delhi NCR. The study was a first-time ever attempt in India using spider webs to assess air quality of urban environment.

MATERIALS AND METHODS

Spider species: The *C. citricola* (Fig. 1) commonly known as the tent-web spider is found in subtropical and tropical areas of Asia, Africa, Australia and in the warm coastal Mediterranean areas of Europe[1]. Though, belongs to the family Araneidae that includes orb-weaver spiders, this species does not build any orb web. Instead, it spins fine-meshed, horizontal, non-adhesive tent webs that form a cone in the middle with many support lines holding it. Unlike orb webs, all cells in its web are rectangular. In the present study, this species was chosen because it is commonly found throughout the region, can live solitary as well as in colony of many individuals and hence, makes large webs and it is available in all types of habitats like road side plantations, human settlements, forests and gardens.

Study area: The study was carried out during January-July, 2015 in the NCR region of Delhi. The web samples were collected during the periods from mid April to mid June at prior identified five different sites (Fig. 2). All samples were brought from residential campus and public parks adjacent to road in case of residential areas and road side vegetation adjacent to industry in case of industrial areas. The sampling locations were mentioned.

Site A: Guru Gobind Singh Indraprastha (GGSIP) University campus, Dwarka, New Delhi. It is a residential area situated in

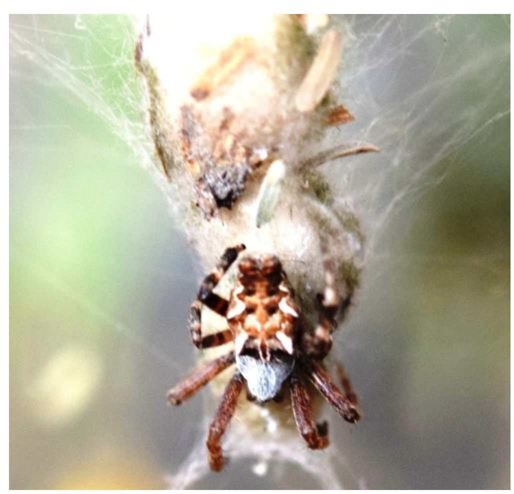

Fig. 1: *Cyrtophora citricola* (Forskål, 1775) inside web

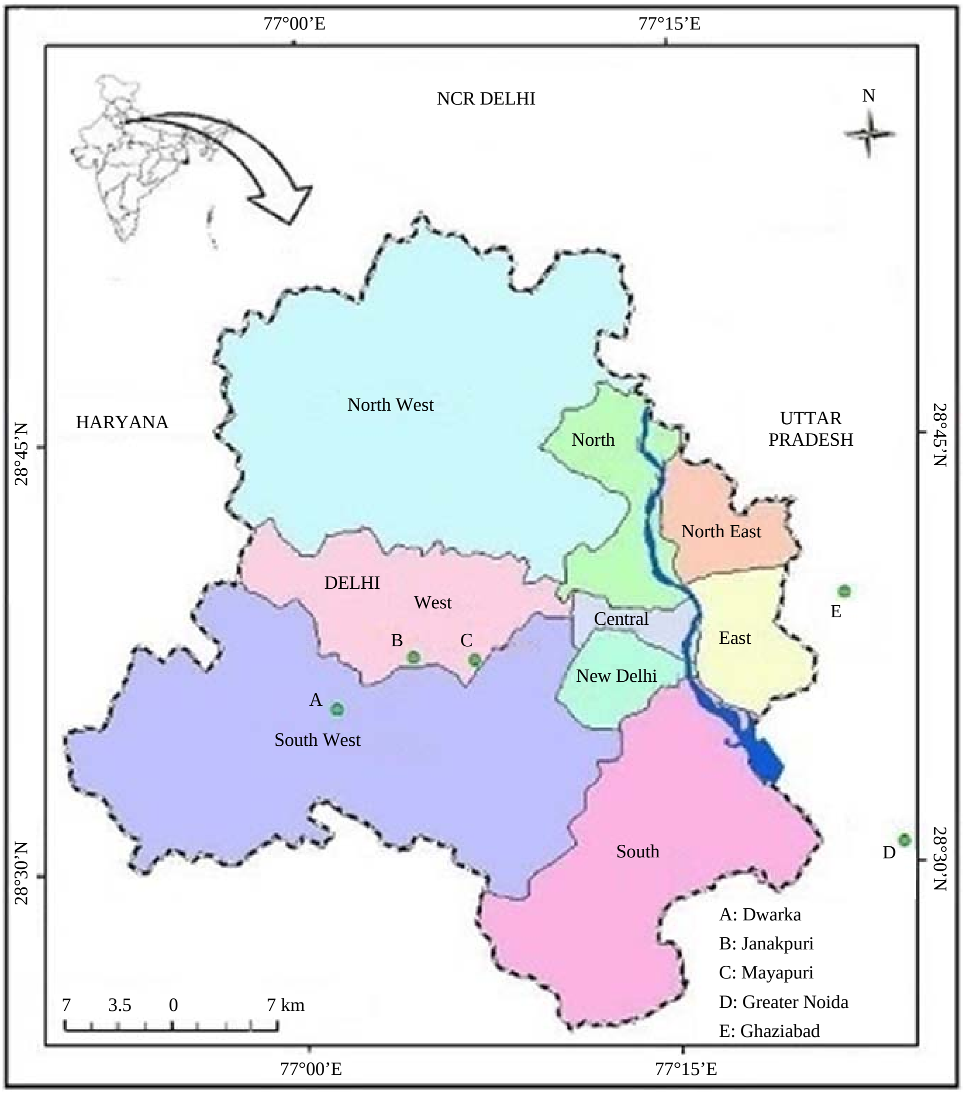

Fig. 2: Study area representing various sampling sites

the outskirts of Delhi and in the vicinity of international airport. The vehicular traffic is low, but the ongoing construction works in nearby areas during the period of sampling may have contributed to the rise in aerosol concentration.

Site B: Janakpuri, New Delhi. It is a residential area. The vehicular traffic load is medium. Asian industries is present in the area which is a leading manufacturer and supplier of chemicals.

Site C: Mayapuri, New Delhi. It used to be a major hub of small scale industries, light metal factories and automobile service stations. It is also one of the major bus terminals for the Delhi Transport Corporation(DTC). Vehicular traffic load is high.

Site D: Greater Noida, Uttar Pradesh. It is commercial-cum-industrial area. Many manufacturing and automobile industries are located in this area. Vehicular traffic load is heavy.

Site E: Ghaziabad, Uttar Pradesh. It is the second largest satellite town in Uttar Pradesh after Kanpur. It is a large and planned industrial hub with primary commercial and industrial center of Western Uttar Pradesh and a major rail junction for North India. Many manufacturing, chemical and textile industries exist in the area. Vehicular traffic is heavy.

Control sample: It was prepared in the laboratory where spiders were fed and allowed to spin silks inside the container to avoid any type of contaminations.

Sampling method: In order to ensure uniformity and comparable age of webs, webs were removed keeping the spiders intact at each identified site 5 days prior to the collection of samples[19]. At each site, webs at a height of 5-7 feet were collected in duplicate from trees. The samples were taken with the help of pipette tips. Tips of pipette were rolled inside webs and web silk was carefully transferred to the clean vials.

Sample treatment: The collected webs were dried at 70°C for 48 h and washed with alcohol to check the greasy matter. Approximately 1 g of webs were weighed on Mettler AT 21comparator balance. Digestion of webs was carried out by treating the weighed webs with ultra-pure concentrated HNO_3 for 40 min at 60°C. The samples were again digested with 2 mL of 30% H_2O_2 and 100 mL of concentrated HNO_3. After digestion, samples were filtered and kept at -20°C till the analysis was performed.

Statistical analysis: Quantitative estimations of the heavy metals proposed in this study were performed by using Agilent 280 FS Atomic Absorption Spectrophotometer (AAS). The samples for the heavy metal analysis were subjected to calibration test for excess curvature using inflection tests with defined error actions. This model of AAS has the typical performance >0.9 absorbance with precision of <0.5% relative standard deviation. All descriptive computations and statistical analyses were done using SPSS software (version 20.0). Heavy metal concentrations between different sampling sites were tested using non parametric Mann-Whitney U-test[27].

RESULTS AND DISCUSSION

In the present study among all the sampling sites, the highest mean concentration of Zn, Pb and Cu were recorded as 2.792, 1.422 and 0.375 μg g^{-1}, respectively at site E and Cd and Ni were recorded as 0.038 and 0.540 μg g^{-1}, respectively at sites D (Table 1, Fig. 3). A significant concentration of Cr was observed in all sampling sites, the highest concentration being at site B followed by site E and A. The mean concentration±SD of all heavy metals (μg g^{-1}) between residential and industrial sites revealed that the concentrations of all heavy metals except Cr were found higher at industrial sites as compared to residential sites (Fig. 4). However, Mann-Whitney U-test showed that there was no significant difference between mean values of heavy metal concentrations between residential and industrial sites (p-value for two tailed including one tailed is 0.113>0.05). In the overall area, mean concentration (μg g^{-1}) of Zn (1.159±0.980) was found to be highest followed by Pb (0.537±0.506), Cr (0.534±0.191), Ni (0.353±0.147), Cu (0.201±0.101) and Cd (0.011±0.016) (Fig. 4). Also, the

Table 1: Mean concentrations of heavy metals (μg g^{-1}) in spider webs collected from different sites and in control sample (N = 12)

Elements	Site A	Site B	Site C	Site D	Site E	Control
Zn	0.565	0.312	0.860	1.268	2.792	0.020
Pb	0.156	0.286	0.419	0.403	1.422	0.010
Cd	0.002	0.001	0.000	0.038	0.012	0.000
Cu	0.145	0.121	0.169	0.194	0.375	0.001
Cr	0.537	0.801	0.443	0.285	0.604	0.001
Ni	0.268	0.154	0.392	0.540	0.411	0.002

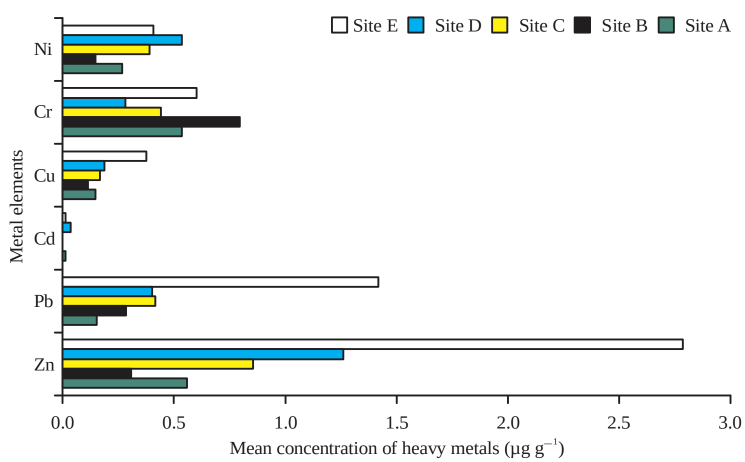

Fig. 3: Mean concentration of heavy metals (μg g^{-1}) in spider webs collected from different sites (N = 10)

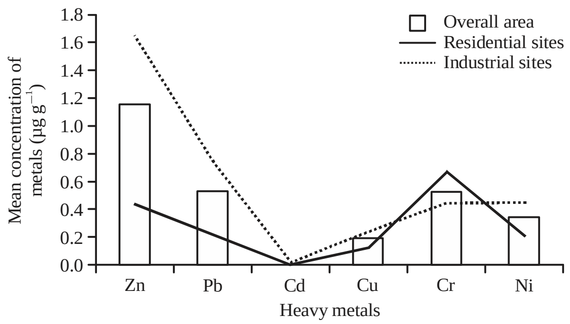

Fig. 4: Mean concentration of heavy metals (µg g^{-1}) in spider webs collected from residential, industrial sites and in overall area

greatest differences between industrial site and residential site were observed for both Zn and Pb concentrations. Nearly 9-fold higher concentration of Zn (site E and B) and Pb (site E and A) was observed at industrial site than residential site (Table 1). Interestingly, very negligible amount (µg g^{-1}) of Zn (0.020), Pb (0.010), Cu (0.001), Cr (0.001) and Ni (0.002) were observed in the webs of control sample that was prepared in the laboratory by keeping live spiders to spin webs inside container (Table 1). Cd was not observed in control sample (Table 1).

The results showed that concentration of all heavy metals except Cr was worse at two industrial sites, D and E in comparison to other sites. Both vehicular pollution as well as industrial activities accounts for higher concentration of heavy metals at these two sites. Sites A and B were residential sites and higher concentration of Cr was recorded from these sites along with one industrial site E. Both vehicular pollution and industrial activity contribute for Cr concentration in ambient air. However, large scale on-going construction work during the study period along with municipal dumps may be the reason for higher concentration of Cr at site A. Similarly, presence of Asian industries at site B may be the reason for higher Cr concentration from this site as this industry is one of the leading manufacturer of industrial chemicals and lacquer. Ayedun *et al.*[10] and Riaz *et al.*[13] have been studied similar heavy metals in air using spider webs and revealed that the concentration of all the heavy metals was higher at all their industrial study sites than residential sites. Though, similar investigation by Rybak[15] has recorded higher concentration of Cr at one residential site as observed in this study. Ayedun *et al.*[10] and Riaz *et al.*[13] have also observed significant difference in the concentrations of heavy metals between industrial sites and residential sites. However, no significant difference in heavy metal concentrations between industrial sites and residential sites was observed in this study that may be due to small sample size. The present study further revealed that the concentration of Zn and Pb in urban air of NCR Delhi is higher in comparison to other heavy metals. Though, all the heavy metals investigated under this study are common in urban atmospheres of this region, higher concentration of Zn and Pb shows that vehicular emission is the major source for suspended particles in air of this region. The result supports findings of Agarwal *et al.*[23], Aneja *et al.*[24] and Goyal and Sidhartha[26]. However, in urban environments of this region, municipal background, engine oil waste, wear and tear of the tyres and corrosion of old buildings are other sources of Zn. Similarly, unleaded fossil fuel sold at filling stations, municipal dumping and break pads of motor vehicles are other sources of Pb. Since, at site E the highest concentration of Zn, Pb and Cu were observed and at this site the maximum, nearly 9-fold higher concentration of Zn and Pb was recorded than residential sites, this indicates that ambient air quality is worst at site E among all the five sites selected in this study. In the present study, presence of a negligible amount of all heavy metals except Cd in the control sample may be due to exposure of spiders to laboratory air at intervals during feeding. Ayedun *et al.*[10] have also revealed similar results in their study though they have not reported about their control sample conditions. Absence of Cd in the control sample was may be due to comparatively lower concentration of this trace element in ambient air of NCR Delhi in comparison to other heavy metals.

Further, it is a common phenomenon in many spiders that they eat their own web regularly to recoup some of the energy used in spinning process and thus their silk proteins are recycled within[3]. Hence, spiders that eat their own web regularly intoxicate some amount of heavy metals regularly in urban environment. However, these spiders have a self-regulatory immunity in the form of metallothioneins (MTs) and detoxifying enzyme system in their body that protect them from stress due to intoxication of heavy metals into their body[11,12,18]. However, during this study *C. citricola* eating of its web was not observed that confirms this species is not a regular eater of its own web and subjected to further verification.

Delhi represents an example of polluted city where the levels of air pollution are in the stage of alarming, posing higher environmental risk to the health of people[23-26]. The city is polluted due to high density of motor vehicles, contaminated landfills and due to its adjacent industrial surroundings. Findings of the present study confirm that spider webs can be used as bioindicator for the indication of heavy metal pollution in urban air of this region. The results support findings of Ayedun *et al.*[10], Riaz *et al.*[13], Rybak and

Olejniczak[14], Rybak[15], Rybak *et al.*[16,17], Xiao-Li *et al.*[19] and Yalwa and Kabo[20]. Rybak and Olejniczak[14] and Rybak *et al.*[17] have also suggested that spider webs are more reliable compared to use of some other bioindicators such as mosses and lichens whose activity is often limited by the lack of water and sunshine. In this direction, conservation of spiders which are efficient bioindicator of heavy metal pollution in urban environment is a challenge due to rapidly changing nature of urban habitats. Also there is a need for more detail study about how spiders can ultimately help in recycling of heavy metals in urban environment as their webs can trap heavy metals which in turn is eaten by them at intervals, but the self-regulatory immunity in their body protect them from stress due to intoxication of such heavy metals.

CONCLUSION

Findings of this study confirm that webs of *C. citricola* can be used as a bioindicator of heavy metal pollution in urban air of NCR Delhi and demands for testing of webs of more such common spiders of this region for their efficiency as bioindicator of heavy metal pollution in air. The study is a pioneer attempt in India to use spider webs to monitor air quality and suggests for long term study with large sample size that will give more accurate picture of effectiveness of spider webs as a tool to indicate seasonal variation in heavy metal pollution of air as well species wise efficiency of webs to be used for such tool in urban environment.

SIGNIFICANCE STATEMENT

Though short term, the findings are promising and confirm that spiders can be used as a conservation tool in any urban environment since their webs can be used as an easily available bioindicator for monitoring of air quality. The findings of this study will no doubt help other researchers to go for testing of webs of common spiders in urban areas to assess their efficiency to monitor air quality of such areas. The study also suggests for use of control sample in such studies for more critical interpretation of findings and demands for more detail study about how spiders can ultimately help in recycling of heavy metals in urban environment.

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