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MONITORING OF HEAVY METALS BY USING PHOLCIDAE SPIDERWEBS IN BASRAH PROVINCE

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Abstract

Key message: The key message of this study is that spiderwebs can be used as an indicator of heavy metal pollution in the air and that industrial and residential areas have higher concentrations of heavy metals compared to agricultural areas with less traffic. The most accumulated heavy metal in spiderwebs was a nickel, followed by zinc, lead, and cobalt in decreasing order. However, comparing the accumulation of heavy metals on spiderwebs to assess air quality was difficult due to the limited number of studies that dealt with it. **Context**: The monitoring of air quality in Basrah province, Iraq, which is known for its oil and gas industry. The study aimed to assess the level of heavy metals in the air using spiderwebs of Pholcidae as an indicator of air pollution. **Aims:** The study aimed to determine the concentrations of four heavy metals (lead, cobalt, nickel, and zinc) accumulated on spiderwebs collected from five different sites in Basrah province. The study also aimed to evaluate the effectiveness of using spiderwebs as a vital indicator of air pollution. **Methods**: The study used spiderwebs of Pholcidae as an indicator of air pollution to determine the concentrations of four heavy metals (lead, cobalt, nickel, and zinc) accumulated on spiderwebs collected from five different sites in Basrah province. The concentrations of heavy metals were determined using atomic absorption spectrophotometry. **Results**: The study found different concentrations of heavy metals in spiderwebs, with heavy-metal concentrations decreasing further away from the road. Industrial and residential areas contained higher concentrations of pollutants than agricultural ones with low traffic. High concentrations of nickel were recorded in most of the study stations, while cobalt had a lower concentration (17.3 µg · g-1 dry weight) than the other heavy metals (nickel, 207.2 µg · g-1; zinc, 133.1 µg · g-1 dry weight; and lead, 45.4 µg · g-1 dry weight) accumulated from the air. **Conclusions:** The study concluded that spiderwebs of Pholcidae can be used as an effective indicator of air pollution, as they can accumulate and retain heavy metals such as lead, cobalt, nickel, and zinc. The study found that the highest concentration of heavy metals recorded in all regions was a nickel, followed by zinc and lead, whereas the lowest concentration was cobalt.

Keywords: Air quality, Heavy metals, Pollution, Spiderwebs, Basrah province, Iraq

1. INTRODUCTION

Basrah is one of the richest provinces in southern Iraq. The environment in Basrah province is exposed to various forms of pollution, including air pollution resulting from many sources. The most crucial pollution sources are the oil industries distributed throughout (Rumaila, Nahran Omar, West Qurna, Majnoon, and Shuaiba), and numerous facilities in large and small industrial areas, such as iron and steel, fertilizer, petrochemical, and electric-power plants (Toamma & AL-Mosuwi, 2021).

Air pollution is the emission of foreign materials in quantities that influence the chemical and physical properties of the air, thereby affecting human health and living organisms (Ogunkunle *et al*., 2015). Bhattacharya *et al*. (2013) explained that most air hazards originate from industrial, residential, and agricultural sources, such as electric power plants, road transport, waste disposal, rapid industrialization, increased emissions, and the movement of cars, especially in urban areas. They contribute to the deterioration of air quality by releasing gases

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and other harmful substances into the atmosphere.

Spiderwebs were used in environmental monitoring for the first time by Yin and Harrison (2000)as an indicator of air pollution. They have been proven effective in accumulating essential atmospheric pollutants, such as (heavy metals) with significant effects on human health and living organisms owing to their susceptibility to high accumulation (Wang & Chen, 2009). Heavy metals are non-biodegradable chemicals that can be associated with the food chain of an ecosystem, and many of them are toxic and carcinogenic. Heavy metals enter the body through inhalation or ingestion of particles or skin absorption (Al-Kasser, 2021).

Lead is one of the most toxic metals owing to its wide-ranging effects on various physiological systems (Jitar *et al*., 2015). The amount of lead absorbed by the lungs is determined by many factors, including air volume, concentration, and age (Al-Hassani, 2013) .Cobalt is used in many industrial applications, such as welding, bullion production, and nuclear power plants. Cobalt enters the human body through food, the respiratory system, and the skin, as it is one of the essential trace elements for the body (Czarnek *et al*., 2015). Zinc is a necessary component of living organisms as it is involved in almost everything, including physiological functions, the production of enzymes and proteins, and DNA repair (Sandstead, 2015). Zinc is closely related to human sources of pollution, such as automobile emissions (Goix *et al*., 2013). Nickel is necessary for small amounts, but it can pose a risk to human health when its absorption is very high. Natural sources of nickel include volcanic eruptions and erosion from rocks and soil. Human exposure to nickel occurs primarily in coal and oil combustion, steelmaking, metal smelting, transportation, and fuel consumption (Dogan *et al*., 2010).

Pholcidae spiders are extensively spread in ecosystems from deserts to forests in rainwater (Huber, 2000, 2001). Pollutants can remain for a long time owing to their physical properties, and spiderwebs can stock up and retain pollutants such as heavy metals. Spiderwebs are found in natural, industrial, and urban settings, including tunnels, roads, and walls of apartment buildings and homes (Rachwał *et al*., 2018).

The research aimed to verify the ability of spiderwebs to accumulate heavy metals to be used as an indicator of the level of air pollution and to determine the concentrations of some heavy metals in the air (e.g., lead, zinc, nickel, and cobalt) to estimate air quality in Basrah Province.

2. MATERIAL AND METHODS

2.1 Study Area

This study was performed in the Iraqi city of Basrah, which is located between 31°30′–29°00′ latitude and 30°48′–46°30′ longitude. The area of the governorate is 19,070 km2, and it constitutes 4.4% of the area of Iraq (NCCI, 2015).

The webs were collected from September 2021 to August 2022 (the study included four seasons (autumn, winter, spring, and summer). Five study stations were selected in Basrah Province, including Abu al-Khasib, Karmat Ali, Shatt al-Arab, the city center, and Rumaila. Three sites were selected for each station, and the regions were determined according to the global

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positioning system, as shown in Figure 1.

2.2 Sampling Design

Spiderwebs of Pholcidea were collected by hand using a wooden stick during the season (winter, spring, summer, and autumn) and placed in clean plastic containers. Then, they were transferred to the laboratory to analyze the heavy-metal concentrations (lead, cobalt, zinc, and nickel). All glassware was washed with deionized distilled water.

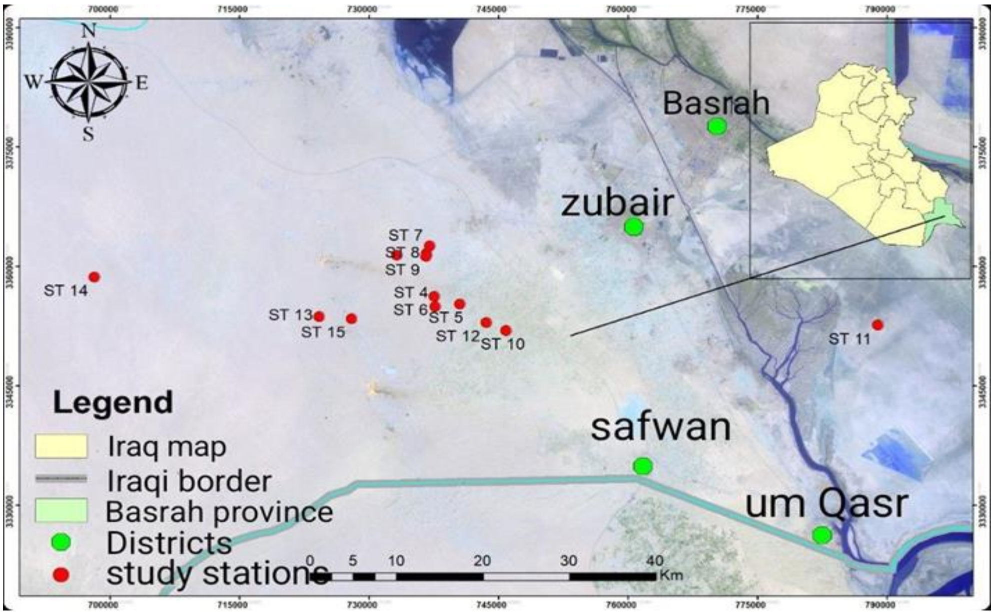

Figure 1: Sample Collection Sites in Basrah Province

2.3 Heavy-metal digestion

After drying the web samples pneumatically in the laboratory, 0.1 g of each sample was weighed in a sensitive balance and then transferred to a digestion flask with a volume of 25 ml to conduct the digestion of heavy metals. The method described by De Wit et al. (1998) was followed in the digestion of heavy metals. Digest the webs in a mixture of 70%-30% of concentrated nitric acid HNO_3 and acid hydrogen peroxide H_2O_2, the acid must be added slowly and carefully, then shake the flask well until it mixes with the sample powder, cover the flasks, and leave for 24 hours under a large vacuum (fume hood) to complete the digestion process. It is then heated at a temperature of 70 degrees Celsius for 2-3 hours on a hot sand plate, then the beakers are removed from the sand plate, and the lid is lifted, then 2-3 ml of non-ionic distilled water is added. Reheat the open flasks in a sand bath at a temperature of 70°C until the volume of the solution is reduced to 2 ml, considering that the solution does not reach dryness. After cooling, transfer to a 50 ml beaker, and complete the volume with deionized distilled water. The solution is centrifuged using clean plastic tubes at 3500 rpm for 30 minutes. The filter is returned to the same volume of 50 ml flask and stored at -20°C. It is ready to measure the concentrations of trace elements using the Flame Atomic Absorption

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Spectrophotometer Type Phoenix-986.

2.4 Statistical analyses

SPSS software (v.24) was used for analysis. All data were analyzed by one-way ANOVA. The significant level for all tests was 0.05.

3. RESULTS

3.1 Diagnostic species

The results of the statistical analysis showed in Table 2. The seasonal and locational variation in the rates of zinc values attached to the webs of Pholcidae spiders in different stations during the study period, as the results of the statistical analysis of the ANOVA, showed that there were significant differences for the seasons (P<0.05 F=80.992, df=3), and the highest value reached 147.26 µg. g-1 dry weight in the summer, and with a significant difference for the stations (P<0.05, F=26.649, df=4), the highest rate was 133.2 µg.g-1 dry weight for the Basra center station. In contrast, the effect of the interference (P<0.05, F= 8.038, df=12) and the highest rate was 258.8 µg.g-1 dry weight for Basra Center Station in the summer.

Table 1: Seasonal zinc (Mean ± SD) in the study stations (µg. g^{-1}) dry weight

Regions	Seasons				Mean ± SD
	Autumn	Winter	Spring	Summer	
Qarmat Ali	42.0±2.9	41.9±6.7	48.1±0.1	85.7±22.6	54.4±21.5
Basra center	41.8±6.8	105.7±8.4	126.5±11.4	258.8±50.2	133.2±85.4
Shatt al-Arab	43.5±15.2	93.8±2.7	104.6±1.67	106.1±8.55	87.0±27.7
Abu al-Khasib	23.6±10.1	47.9±19.4	92.1±9.02	126.5±24.62	72.5±43.95
Rumaila	39.1±11.6	66.9±14.2	57.5±22.86	159.2±44.0	81.9±55.7
Mean ± SD	38.03±11.54	71.5±28.4	85.8±31.9	147.26±69.0	

The concentrations of zinc varied between the stations during the current study semesters. The highest concentration rate in the Basrah Center station was 133.2 µg. g-1 dry weight. These high levels of zinc are related to heavy traffic, the number of industries and activities in the concerned areas, lubricants, engines, tires, and Brake lining erosion Al-Sareji et al. (2021), as well as the role of wind in transporting pollutants from different areas and depositing them in the study area and to the proximity of the area to the main road and weather conditions such as rainfall, it may be related to the predominance of northwest winds. In comparison, the lowest rate of zinc concentration in the Qarma station was 54.4 µg. g-1 dry weight. The reason for the low concentration of zinc is since this area has little industrial activity and is a distance from the main road; all stations have exceeded the upper limit allowed for zinc in the air, according to the World Health Organization (WHO, 1996) and the amount of 6 mg / m3. The statistical analysis results (Table 3) showed the seasonal and locational variation in the rates of lead values attached to Pholcidae spider webs at different stations during the study period. The results of the statistical analysis of the ANOVA table showed that there were significant differences for the seasons (P<0.05, 136.046F=, 3df=), the highest value of which was 148.38 µg.g-1dry weight in the summer season, with a significant difference for the stations (P<0.05,

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F=28.349,df=4), the highest rate was 145.4 µg.g-1 dry weight for the Basra Center station, but the effect of the interference ($P<0.05$, F=3.755, df=12), the highest rate was 76.1 µg.g-1 dry weight for Basra Center Station in the spring. This study showed the regional variation in lead concentration in spiderwebs as lead values were increased in the Basrah Center Station. Lead is a common metal for vehicle emissions worldwide, although it has been removed from most gasoline products (Xiao et al., 2006; Gugamsetty et al., 2012).

Our finding agreed with that of Amtehgy et al. (2015), who found that the amount of metal decreases with increased distance from the road, so the lead level drops sharply. The high lead concentration is attributed to the lead particles produced by the combustion of gasoline, which settles on the side of the road. Vehicles often move slowly due to traffic congestion, which may explain the high level of lead in the city center. In our study, the average concentration of lead in the center of Basrah was 145.44 µg·g–1 dry weight. In the study of Amtehgy et al. (2015), the highest street lead level is recorded as 350 µg·g–1 dry weight resulting from busy roads and surrounding human activities. The statistical analysis results showed Table 4 seasonal and locational variation in the rates of nickel values attached to Pholcidae spider webs at different stations during the study period. The results of the statistical analysis of the ANOVA table showed that there were significant differences for the seasons ($P<0.05$, F= 58.338, df=3), and the highest value was 142.5 µg.g-1 dry weight in the winter season, with a significant difference for the stations ($P<0.05$, F=93.4, df=4), the highest rate was 205.8 µg.g-1 dry weight for Rumaila station, while the effect of interference ($P<0.05$, F=7.515, df=12). The highest rate was 266.0 µg.g-1 dry weight for Rumaila station in winter.

Table 2: Seasonal zinc (Mean ± SD) in the study stations (µg. g^{-1}) dry weight

Regions	Seasons				Mean ± SD
	Autumn	Winter	Spring	Summer	
Qarmat Ali	BDL	16.6±2.3	29.1±2.0	37.2±1.1	20.9±14.7
Basra center	5.9±1.0	35.0±11.1	76.1±16.6	64.7±6.0	45.4±29.9
Shatt al-Arab	BDL	8.2±6.3	29.1±4.0	35.9±11.1	18.3±16.3
Abu al-Khasib	2.7±2.9	8.7±8.9	44.3±6.0	48.3±7.0	26.0±22.1
Rumaila	7.0±2.9	27.1±8.6	42.3±1.14	55.5±10.8	32.9±19.8
Mean ± SD	3.12±3.42	19.14±12.81	44.2±19.08	48.38±13.2	

BDL: Below the detection limit

Table 3: Seasonal variation of lead (Mean ± SD) in the study stations (µg. g^{-1}) dry weight

Regions	Seasons				Mean ± SD
	Autumn	Winter	Spring	Summer	
Qarmat Ali	BDL	16.6±2.3	29.1±2.0	37.2±1.1	20.9±14.7
Basra center	5.9±1.0	35.0±11.1	76.1±16.6	64.7±6.0	45.4±29.9
Shatt al-Arab	BDL	8.2±6.3	29.1±4.0	35.9±11.1	18.3±16.3
Abu al-Khasib	2.7±2.9	8.7±8.9	44.3±6.0	48.3±7.0	26.0±22.1
Rumaila	7.0±2.9	27.1±8.6	42.3±1.14	55.5±10.8	32.9±19.8
Mean ± SD	3.12±3.42	19.14±12.81	44.2±19.08	48.38±13.2	

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BDL: Below the detection limit

This study showed the regional variation in lead concentration in spiderwebs as lead values were increased in the Basrah Center Station. Lead is a common metal for vehicle emissions worldwide, although it has been removed from most gasoline products (Xiao et al., 2006; Gugamsetty et al., 2012). Our finding agreed with that of Amtehgy et al. (2015), who found that the amount of metal decreases with increased distance from the road, so the lead level drops sharply. The high lead concentration is attributed to the lead particles produced by the combustion of gasoline, which settles on the side of the road. Vehicles often move slowly due to traffic congestion, which may explain the high level of lead in the city center. In our study, the average concentration of lead in the center of Basrah was 145.44 µg·g–1 dry weight. In the study of Amtehgy et al. (2015), the highest street lead level is recorded as 350 µg·g–1 dry weight resulting from busy roads and surrounding human activities. The statistical analysis results showed Table 4 seasonal and locational variation in the rates of nickel values attached to Pholcidae spider webs at different stations during the study period. The results of the statistical analysis of the ANOVA table showed that there were significant differences for the seasons ($P<0.05$, $F= 58.338$, $df=3$), and the highest value was 142.5 µg.g-1 dry weight in the winter season, with a significant difference for the stations ($P<0.05$, $F=93.4$, $df=4$), the highest rate was 205.8 µg.g-1 dry weight for Rumaila station, while the effect of interference ($P<0.05$, $F=7.515$, $df=12$). The highest rate was 266.0 µg.g-1 dry weight for Rumaila station in winter.

This study recorded changes in nickel concentration, where the highest concentration of nickel metal in Rumaila was 207.2 µg·g–1 dry weight because this area is industrial and is characterized by the abundance of oil facilities. For gravel and sand, the lowest percentage was recorded in the Shatt Al-Arab station with a concentration of 67.3 µg·g–1 dry weight. By comparing the results of this study with those of Radhi et al. (2021), we found that nickel concentration in gray dust was 100.05 µg·g–1 dry weight, whereas in the current study, the nickel concentration was high, i.e., 265.9 µg·g–1 g-1 dry weight. Ayedun et al. (2013) explained that the average values of nickel concentration in industrial areas range between 0.004–0.02 µg·g–1, and the average values of nickel concentration in residential areas are 0.01–0.03 µg·g–1. The statistical analysis results showed in Table 5 the seasonal and local variation in the rates of cobalt values attached to Pholcidae spider webs in different stations during the study period. The results of the ANOVA table's statistical analysis showed significant differences for the seasons ($P<0.05$, $F=15.746$, $df=4$). The highest value was 11.9 µg .g-1dry weight in the winter season, with a significant difference for the stations ($P<0.05$), $F = 9.119$, $df=3$), the highest rate was 17.3 µg .g-1dry weight for the Basra center station, while the interference effect ($P<0.05$, $F=2.744$, $df=12$). In winter, the highest rate reached 22.7 µg .g-1 dry weight at the Basra center station.

Results showed that cobalt concentration increased in the stations of the Basrah Center and Rumaila. The Basrah Center station recorded the highest spiderweb cobalt concentration, 17.3 µg·g–1 dry weight. This increase may result from manufacturing, waste burning, and vehicle emissions. In contrast, the current study recorded low rates of cobalt in the Shatt Al-Arab and Qarma Ali stations (4.5 and 5.7 5 µg·g–1 dry weight). Cobalt recorded a lower rate than the other heavy metals (lead, nickel, and zinc) accumulated from the air in the study stations. This finding agreed with that of Al-Dabbas et al. (2018). They found that cobalt metal concentrations ranged from 4 µg·g–1 in 10 locations to 18 µg·g–1 in the dust of the Diwaniyah Governorate. This concentration was close to the cobalt concentration in the current study.

Table 4: Seasonal Nickel concentration (Mean ± SD) in the study stations (µg. g-1) dry weight

Regions	Seasons				Rate for Stations
	Autumn	Winter	Spring	Summer	
Qarmat Ali	BDL	64.2±1.31	85.7±0.6	136.7±25.8	71.7±52.4
Basra center	51.5±10.6	184.4±28.9	149.2±43.5	133.9±7.6	129.5±55.8
Shatt al-Arab	17.4±20.9	64.2±17.2	98.0±15.5	90.0±3.3	67.4±35.4
Abu al-Khasib	75.6±27.7	133.5±9.3	51.3±12.7	121.0±35.0	95.3±40.2
Rumaila	145.8±12.6	266.0±5.4	194.0±3.4	223.3±36.7	205.8±49.4
Rate for seasons	58.0±54.8	142.5±80.4	115.6±55.0	134.9±46.0	

BDL: Below the detection limit

Table 5: Seasonal Cobalt concentrations (Mean ± SD) in the study stations (µg. g^{-1}) dry weight

Regions	Seasons				Mean ± SD
	Autumn	Winter	Spring	Summer	
Qarmat Ali	5.3±0.4	BDL	8.9±0.4	4.1±4.0	4.5±3.73
Basra center	10.1±10.5	22.7±1.24	16.5±8.4	19.8±3.9	17.3±7.73
Shatt al-Arab	1.9±0.7	6.3±2.8	9.3±0.8	5.3±0.8	5.7±3.05
Abu al-Khasib	7.7±5.2	5.0±4.8	14.0±4.6	12.1±4.0	9.7±5.48
Rumaila	3.5±2.2	3.2±5.6	15.0±5.4	18.0±0.6	9.9±7.77
Mean ± SD	5.7±5.4	7.46±8.7	13±5.2	11.9±7.1	

BDL: Below the detection limit

4. CONCLUSION

This study was the first to monitor the level of heavy metals in the air in Iraq. The study concluded that spiderwebs of Pholcidae can be used as an effective indicator of air pollution, as they can accumulate and retain heavy metals such as lead, cobalt, nickel, and zinc. The study found that the highest concentration of heavy metals recorded in all regions was a nickel, followed by zinc and lead, whereas the lowest concentration was cobalt.

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Code Availability

Not applicable

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Reference to preprint servers

Not applicable

Authors' Contributions

The study was conceived and planned by Nayyef Azeez and Shurooq A. Najim conducted the fieldwork. Huda Z. Taher prepared the datasets and performed the analysis and wrote the manuscript. The authors read and approved the final manuscript.

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Availability of data and materials

Declarations

Ethics Approval and Consent to Participate

Not applicable. All authors gave their informed consent to this publication and its content.

Competing Interests

The authors declare that they have no competing interests.

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