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The use of spider webs for environmental determination of suspended trace metals in industrial and residential areas

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Spider webs were collected from industrial and residential areas in order to establish the level of suspended heavy metals in the atmosphere. The spider webs were treated with nitric acid and digested before analysis using atomic absorption spectrophotometer (AAS). The mean concentration value of some heavy metals were found to be significantly high at p < 0.05 in suspended particles in industrial areas namely, Lead (Pb) 0.53 ± 0.09 and Cadmium (Cd) $0.15 \pm 0.05 \ \mu gg^{-1}$, respectively. The mean concentration values of Zinc (Zn), Nickel (Ni) and Copper (Cu) were not significantly different from industrial, residential and control sites. It was found that, the concentration of heavy metals decreases as the web samples were collected further away from the road.

Key words: Metals, spider, webs, indicator, environment.

INTRODUCTION

Monitoring trace metals in street dust has provided a tool for estimating the degree of contamination, source and habitat of residential commercial and industrial areas. Industrial street dust and motor vehicle emissions are sources of airborne particulates in urban environment (Kowalczyk et al., 1982). The particles emitted by motor vehicles carry or contain heavy metals that may be toxic when present in excess of natural background levels (Gertler et al., 2000). The toxic properties of this airborne particulate may be due to the biochemical activity of metals attached to them (Smith and Aust, 1997). The ingredient present in domestic airborne aerosol plays a significant role in toxicological effects. Being sufficiently small and insoluble, these would get adequate time to penetrate the deepest area of lungs triggering asthma attacks and aggravate suffering (Smith and Aust, 1997). Webs of species of spider, Stiphidion facetum, were commonly found in both natural and built structures on trees, rocks, fallen logs, under bridges and wall of caves (Marples, 1976; Hickman, 1967). The web of this spider is a densely woven sheet of cribellate silk which hangs

like a hammock, attached to the substrate by supporting threads at several points around circumference. The spiders continually repair their webs but if badly damaged or removed, they build another web; thus, webs are renewable and may be useful for assessing temporal change. Zmudzki and Laskowski (2012) studied the biodiversity and structure of spider communities along a metal pollution gradient and concluded that spider's community may be affected by heavy metals not only directly, but also by indirect effect of pollutants.

The level of heavy metals in spider webs can be used for both quality control and also for determination of environmental contamination or pollution. Spider webs have been demonstrated as effective indicator of heavy metals attributed to particulate emission (Hose et al., 2002). In most developing countries, monitoring pollution may be too expensive because of the economic situation. If the instrument for monitoring is available, handling and maintenance may pose a problem because the maker may not take into consideration the weather condition of the country. Therefore, there is a need to look for inexpensive way of monitoring trace metals in our environment. The aim of the present study is to assess the quality of air in industrial and residential environment using spider webs as an indicator.

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MATERIALS AND METHODS

Sampling area

Ota city is the industrial nerve centers of Ogun State, lying between latitude 6° 42′ 0″ N and longitude 3° 13′ 47″ E. Three industrial areas were ldiroko road, Lagos-Abeokuta express way and ljoko road, respectively. The residential areas consist of Ota, Sango and ljoko, while the control sites consists of farmlands within Federal Polytechnic Ilaro, along Oja Odan road where no human settlements and industrial activities occur with the exception of few vehicular passage on the road. Ilaro is located on latitude 6° 42′ 0″ N and longitude 3° 13′ 47″ E.

Sample collection

Spider webs were collected from industrial and residential areas of Ota Ogun State, Southwest, Nigeria. These spider webs were collected during dry season (January/February, 2011). To ensure uniform and comparable age of the webs at each site, the webs were identified and harvested after 7 days (Xiaoli et al., 2006).

Sample treatment

The collected webs were washed with alcohol to remove greasy matter, air-dried, digested by treating 1 g of each web with concentrated nitric acid and boiled, re-dissolved and boiled for 6 h. Samples were re-suspended in nitric acid and 2.0 ml of 30% hydrogen peroxide. The residue was repeatedly re-suspended in nitric acid and heated at 120°C until digestion was complete.

Sample analysis

Quantitative determination of the trace metals was performed by an Atomic Absorption Spectrophotometer (AAS) (Bulk Scientific Model).

Statistical analysis

Data were analyzed using one way analysis of variance.

RESULTS AND DISCUSSION

Table 1 showed detailed results obtained from different locations. The highest mean Lead (Pb) concentration values of 0.44, 0.62, and 0.53 μ gg⁻¹ was recorded in industrial areas A, B and C, respectively. The mean Pb values of 0.06, 0.05, and 0.01 μ gg⁻¹ was recorded from residential areas D, E and F, respectively, while value of 0.02 μ gg⁻¹ was recorded each for control sites G, H and I, respectively. Similarly, the mean Cadmium (Cd) concentration values of 0.11, 0.14, and 0.20 μ gg⁻¹ was recorded from residential areas, while 0.04, 0.04, and 0.03 μ gg⁻¹ was recorded from the control sites. The mean values of Zinc (Zn) concentration from industrial areas are: 0.35, 0.18, and 0.18 μ gg⁻¹, respectively, while those from residential areas are: 0.27, 0.18, and 0.18 μ gg⁻¹,

respectively. The mean Zn concentration values of 0.01 μ gg⁻¹ each was recorded from the control sites. The mean values of Nickel (Ni) concentration from industrial areas are: 0.0.04, 0.02, and 0.01 μ gg⁻¹, respectively, while those from residential areas are 0.01, 0.01, and 0.03 μ gg⁻¹, respectively. The mean Ni concentration values of 0.01 μ gg⁻¹ each was recorded from the control sites. The mean values of Copper (Cu) recorded from both industrial, residential and control sites are almost the same with the mean value of 0.01 μ gg⁻¹ recorded from all locations (Table 1).

Table 2 showed the statistical analysis of results of metal samples analyzed from spider webs collected from industrial, residential and control sites. There was a significant difference in concentration of Pb and Cd from industrial and residential areas, whereas there was no significant difference in concentration of Zn, Ni and Cu from both industrial, residential and control sites. Similarly, Figures 1, 2 and 3 showed the variations of metal concentrations from various distances to the high way.

The highest concentration of Pb, Cd, Zn, Ni and Cu are 0.98, 0.42, 0.52, 0.05 and 0.03 µgg⁻¹, respectively, as recorded from Locations A, C, A, A, and B which are all industrial locations (Table 1). This fact was further corroborated by the results of statistical analysis which showed that the concentrations of Pb was significantly higher in spider web samples collected from industrial areas with the mean value of 0.53 \pm 0.09 µgg⁻¹, while there was no significant difference in the mean values of Pb recorded from residential and control locations (Table 2). Similarly, Cd concentration was significantly higher at P < 0.5 in industrial areas with the mean value of 0.15 ± 0.05 µgg⁻¹, whereas no significant difference in mean values was recorded from residential and control sites. However, for Zn, Ni and Cu, there was no significant difference. The values recorded for Pb may be due to industrial activities in the area but the fact that appreciable values are recorded in the residential and control sites simply indicates that Pb in suspended particles are ubiquitous showing how unsafe the air we breadth-in were. Accumulation of metals especially Pb, by spiders in these locations is likely to occur. Hendrickx et al. (2004), and Laskowski and Kammenga (2000) reported spider as one of the terrestrial invertebrates that accumulate the highest concentrations of many trace metals. When intoxicated with metals they exhibit strong physiological reactions due to the intoxication, for example, by having elevated levels of detoxifying enzymes which may lead to shifts in their energy budgets (Babczynska et al., 2006; Wilczek et al., 2003, 2004). Xiaoli et al. (2006) reported the mean concentration of Pb of 4.5 times greater from different locations and significantly high value at P < 0.05 in spider webs. However, particulate emissions from motor vehicle are a probable source (De Miguel et al., 1997; Sternbeck et al., 2002). With the removal of Pb from most petrol

Element	Α	В	С	D	Е	F	G	н	I
Pb									
1	0.98	0.92	0.73	0.09	0.08	0.02	0.03	0.02	0.03
2	0.27	0.52	0.62	0.06	0.07	0.01	0.02	0.02	0.01
3	0.08	0.42	0.25	0.02	0.01	0.01	0.01	0.01	0.01
Mean	0.44	0.62	0.53	0.06	0.05	0.01	0.02	0.02	0.02
<u>.</u>									
Cd	0.47	0.00	0.40	0.04	0.07	0.00	0.00	0.00	0.00
1	0.17	0.22	0.42	0.04	0.07	0.06	0.02	0.02	0.02
2	0.13	0.12	0.11	0.05	0.02	0.02	0.01	0.01	0.01
3	0.04	0.09	0.08	0.02	0.01	0.01	0.01	0.01	0.01
Mean	0.11	0.14	0.20	0.04	0.03	0.03	0.01	0.01	0.01
7n									
1	0.52	0.37	0.31	0.37	0.22	0.12	0.02	0.02	0.02
2	0.45	0.15	0.22	0.33	0.21	0.11	0.01	0.01	0.01
3	0.07	0.03	0.01	0.12	0.1	0.01	0.01	0.01	0.01
Mean	0.35	0.18	0.18	0.27	0.18	0.08	0.01	0.01	0.01
Ni									
1	0.05	0.03	0.02	0.01	0.02	0.05	0.02	0.01	0.01
2	0.04	0.02	0.01	0	0.01	0.02	0.01	0.01	0.01
3	0.03	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01
Mean	0.04	0.02	0.01	0.01	0.01	0.03	0.01	0.01	0.01
_									
Cu									
1	0.02	0.03	0.02	0.02	0.01	0.01	0.02	0.01	0.01
2	0.01	0.01	0.01	0.01	0	0.01	0	0.01	0.01
3	0.01	0	0.01	0.01	0	0	0	0	0
Mean	0.01	0.01	0.01	0.01	0.003	0.01	0.01	0.01	0.01

Table 1. Detailed results of concentration (μ gg⁻¹) of elements measured in spider webs collected from different industrial (A, B, C), residential (D, E, F) and control sites (G, H, I) (N = 27).

Table 2. Distribution of concentration \pm SD (μ gg⁻¹) of elements measured in spider webs collected from different industrial, residential and control sites (N = 27).

Location	Pb	Cd	Zn	Ni	Cu
Industrial	0.53 ± 0.09^{b}	0.15 ± 0.05^{b}	0.24 ± 0.10^{a}	0.02 ± 0.01^{a}	0.01 ± 0.00^{a}
Residential	0.04 ± 0.03^{a}	0.03 ± 0.01^{a}	0.18 ± 0.10^{a}	0.02 ± 0.01^{a}	0.01 ± 0.00^{a}
Control	0.02 ± 0.00^{a}	0.01 ± 0.00^{a}	0.01 ± 0.00^{a}	0.01 ± 0.00^{a}	0.01 ± 0.00^{a}

Superscripts with the same letters down the column are not significantly different according to Duncan Multiple Range Test (P < 0.05).

worldwide, combustion of fuels is now an insignificant source of Pb emissions, but may contribute Zn and Cd (Sternbeck et al., 2002). The source of Pb in Nigerian oil is likely due to emergence of illegal refineries which used outlawed methods [for example, tetra ethyl lead (TEL)] in the refining of crude oil and smuggling of their products into the Nigerian market. Brake linings are now the most

common source of Pb in roadside environments, although re-suspension of Pb contaminated dusts remain an issue (De Miguel et al., 1997). Wear of brake linings is the principal sources of Cu, and the wear of tyres and motor oils are considered the primary sources of Zn (Sternbeck et al., 2002).

Consider the distance of sample location to the main



Figure 1. Variation of metal concentrations at 100 m from road.



Figure 2. Variation of metal concentrations at a distance of 200 m from road.



Figure 3. Variation of metal concentrations at a distance of 300 m from road.

road where vehicular activities occur on a regular basis; Figures 1, 2, and 3 showed variation of elements under consideration and their various concentrations. At all the distances away from the main road, the order of concentration was Pb > Zn > Cd > Ni > Cu (Figures 1, 2, and 3). The concentration of Pb at 100, 200, and 300 m were, 0.34, 0.18, and 0.09 μ gg⁻¹, respectively, showing that proximity of the sample location to the very busy road is a primary factor. Horse et al. (2002) collected webs from reference sites that were more than 30 km from the nearest major road. Xiaoli et al. (2006) reported webs that contained 100 μ g/g of Zn and 30 μ g/g of Pb which are less than the concentration recorded in urban reference sites.

These findings for Pb, Zn, and Cd are consistent with previous studies that have shown a decrease in metal concentrations with increasing distance from the road (Yassoglou et al., 1987). This may be explained by De Nevers (1999) who showed that about 40% of particulate emissions have diameters larger than 9 µm that because of their high gravitational settling velocity, settle quickly and are deposited within about 10 m from the road. About 20% of the particles have diameter between 1 and 9 µm and are deposited about 40 m from the road. The remaining 40% of the particles have diameters less than 1 µm and remain suspended in the atmosphere for a long time and may be carried far away from the road. Most Cu is associated with particles 1 to 10 µm in size (Lough et al., 2005) with a mean particle size of 6 µm (Sanders et al., 2003).

The difference in concentration among the sites simply reflects differences in the ages of webs from each site. Effort was made to sample the webs of matured spiders in an attempt to make size and age ranges of webs from each site as comparable as possible. The significance of knowing the web age as used in the present study is that it provides a specific age of the web as webs accumulate heavy metal loads over a period of time, which gives webs a distinct advantage over conventional air sampling strategies (such as dynamometric tests) that only provide a snapshot of conditions.

Conclusion

In this study, we investigated concentration of metals in suspended particles in spider webs from industrial and residential areas. The concentration of metals in spider webs from the study area is not only caused by industrial activities but vehicular movement contributed largely to the values recorded. Effort should be intensified to monitor vehicular emission on a regular basis in order to ensure safe environment.

REFERENCES

- Babczynska A, Wilczek G, Migula P (2006). Effects of dimethoate on spiders from metal pollution gradient. Sci. Total Environ. 370:352-359.
- De Miguel E, Llamas JF, Chacon E, Berg T, Larssen S, Royset O, Vadset M (1997). Origin and patterns of distribution of trace elements in street dust: Unleaded petrol and urban lead. Atmos. Environ. 31:2733-2740.
- De Nevers N (1999). Air pollution control engineering. McGraw-Hill, London, England pp. 221-249.
- Gertler AW, Gillies JA, Pierson WR (2000). An assessment of the mobile source contribution to PM 10 and PM 25 in the United States. Water Air Soil Pollut. 123:203-214.
- Hendrickx F, Maelfait JP, Bogaert N, Tojal C, Du Laing G, Tack FM,

Verloo MG (2004). The importance of biological factors affecting trace metal concentration as revealed from accumulation patterns in co-occurring terrestrial invertebrates. Environ Pollut. 127:335-341.

Hickman VV (1967). Some common spiders of Tasmania. Tasmania Museum and Art Gallery, Hobart, Tasmania. 113:53-79.

Hose GC, James JM, Gray MR (2002). Spider webs as environmental Indicators. Environ. Pollut. 120:725-733.

Kowalczyk GS, Gordon GE, RheinGrover SW (1982). Identification of atmospherical particulate sources in Washington, D. C. using chemical element balances. Environ. Sci. Tech. 16:79-90.

Laskowski R, Kammenga J (2000). Demography in ecotoxicology. Wiley, New York. pp. 57-71.

Lough GC, Schauer JJ, Park JS, Shafer MM, Deminter JT, Weinstein JP (2005). Emissions of metals - associated with motor vehicle roadways. Environ. Sci. Technol. 39:826-836.

Marples BY (1976). The Dictynid spiders of New Zealand. Transactions of the Royal Society of New Zealand. 87(3-4):333-361.

Sanders PG, Xu N, Dalka TM, Maricq MM (2003). Airborne brake ware debris: Size distributions, composition and a comparison of dynamometer and vehicle tests. Environ. Sci. Technol. 37:4060-4069.

Smith KR, Aust AE (1997). Mobilization of iron from urban particulates leads to generation of reactive oxygen species *in vitro* and induction of ferritin synthesis in human during epithelia cells. Chem. Res. Toxicol. 10:824-834.

Sternbeck J, Sjodin A, Andreasson K (2002). Metal emission from road Traffic and the influence of resuspension-results from two tunnel studies. Atmos Environ. 36:4735-4744. Wilczek G, Babczyn ska A, Augustyniak M, Migula P (2004). Relations between metals (Zn, Pb, Cd and Cu) and glutathione-dependent detoxifying enzymes in spiders from a heavy metal pollution gradient. Environ. Pollut. 132:453-461.

Wilczek G, Babczyn'ska A, Migula P, Wencelis B (2003). Activity of esterases as biomarkers of metal exposure in spiders from the metal polluted gradient. Pol. J. Environ. Stud. 12:765-771.

Xiaoli S, Yu P, Hose GC, Feng-Xiang L (2006). Spider webs as indicators of heavy metal pollution in air. Bull. Environ. Contam. Toxicol. 76:271-277.

Yassoglou N, Kosmas C, Asimakopolous J, Kallianou C (1987). Heavy metal contamination of roadside soils in the greater Athens area. Environ. Pollut. 47:293-304.

Zmudzki S, Laskowski R (2012). Biodiversity and structure of spider communities along a metal pollution gradient. Ecotoxicology 21:1523-1532.