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SPIDER WEBS AS NATURAL SAMPLERS

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ABSTRACT

Spider webs collected from the indoor and outdoor of 120 sampling sites of 10 zones of Kano Municipality were analysed for manganese and iron by the use of Atomic Absorption Spectrophotometery (AAS), after digestion in the mixture of concentrated nitric acid and hydrogen peroxide. The analysis of the webs showed different levels of the metals in the indoor and outdoor samples with means and standard deviations of 273.33±133.98 and 378.33±159.06 µg/g, for manganese indoor and outdoor respectively, then 3083.33±1314.00 and 4200.00±1656.00µg/g for iron indoor and outdoor respectively. These variations in concentrations have been attributed to emissions from dust particles, motor vehicle/industrial emissions and other activities in the metropolis. Analysis of the webs also showed large differences between the sites which could be attributed to the geology and human activities in each locality. Spider webs analysis has thus proved to be accumulators and therefore useful indicators of pollutants of the environment from which they were collected, hence can be used as natural samplers.

Keywords: spider, sampler, manganese, iron, pollution, Kano.

INTRODUCTION

Manganese is essential for the activities of many enzymes (Hill and Holman, 1980); it is an essential component of over thirty-six enzymes that are used for the carbohydrate, protein and fat metabolism (Lenntech, 2009). Mammals can have 1-3ppm in their tissues (Lenntech, 2009). Its concentration in human plasma has been reported as 9.37-11.36µg/g (Nosolodin and Rusin, 1980). Manganese is needed for the function of ovaries and testes and as an activator of certain enzyme systems (Schmidt-Nielsen, 1995). The uptake of manganese by humans takes place through food, such as spinach, tea and herbs. The foodstuffs containing the highest concentrations are grains, rice, soya beans, eggs, nuts, olive oil, green beans and oysters. Manganese deficiency symptoms include abnormal development of the bones (Schmidt-Nielsen, 1995). With animals that eat too little manganese, interference of normal growth, bone formation and reproduction will occur. The deficiency can also cause fatness, glucose intolerance, blood clotting, skin problems, lowered cholesterol levels, skeleton disorders, birth defects, changes of hair colour and neurological symptoms (Lenntech, 2009). Manganese is an essential element, however, toxic on exceeding its threshold limit. Its effects occur mainly in the respiratory tract and the brains. Symptoms of manganese poisoning are hallucinations, forgetfulness and nerve damage (Lenntech, 2009). Manganese can cause Parkinson's, lung embolism and bronchitis (Finkelstein and Jerrett, 2007). When men are exposed to manganese for a longer period of time they may become impotent (Lenntech, 2010). A syndrome that is caused by manganese has symptoms such as schizophrenia, dullness, weak muscles, headaches and insomnia (Sanders, 2010). When manganese uptake takes place through the skin it can cause tremors and coordination failures. In plants manganese is essential in the food manufacture and its deficiency can cause disturbances in the plant mechanisms. Highly toxic concentrations of manganese in soils can cause swelling of cell walls, withering of leafs and brown spots on leaves. Manganese particles in air are present as dust particles. Humans enhance manganese concentrations in the air by industrial activities and through burning fossil fuels. Manganese derived from human sources can enter surface, ground and sewage water and also enter soil through the application of manganese pesticides (Lenntech, 2009).

Iron is ubiquitous in living systems; it is found in the whole gamut of life forms from bacteria to man. It is the second most abundant metal and fourth most abundant element in the earth's crust. It is readily interconverted into any of its two states and this has led to its evolutionary selection for use in many life processes (Cotton *et al.*, 1999). It is essential in the formation of red blood cells, liver and spleen (Bowen, 1960). It forms an important constituent of haemoglobin (O'Dell and Cambell, 1971). It is at the active centre of molecules responsible for oxygen and electron transport, and is found in, or with, such diverse metalloenzymes as various oxidases, hydrogenases, reductases, dehydrogenases, deoxygenases and dehydrases (Cotton *et al.*, 1999). The total amount of iron in an adult human is about 4.0-6.0g and of this amount 70% is found in heamoglobin, 3.2% in myoglobin, 0.1% in cytochromes, 0.1% in catalase, and the remainder in storage compounds mostly in the liver (Schmidt-Nielsen, 1995; Cotton *et al.*, 1999). Low blood iron or anaemia is caused by either inadequate intake or if its metabolism is impaired (Dallham *et al.*, 1982). The total iron content of the human body varies with age, sex, nutrition and state of health (Wells and Awad, 1992). Iron is, however toxic if taken from sources outside the normal food supply (Sandy and Richard, 1989). In the air, iron causes respiratory cancer (Smith *et al.*, 1987). Iron in the air exists mainly as iron III compounds from soil, iron and steel works, rolling mills, municipal waste etc. (Cotton *et al.*, 1999), and automobiles (Yeung *et al.*, 2003).

Spiders are the largest group of arachnids (Pestproducts, 2008; Sebastin and Peter, 2009) and rank seventh in total species diversity among all other groups of organisms; with 109 families of about 40,000 species (Sebastin and Peter, 2009), therefore found in all parts the world. Almost all spiders are predators, feeding mostly on insects, although some spiders capture and eat tadpoles, small frogs, small fish and mice (Dunne and Eiscabeis, 1980) and a few large species take birds and lizards (Ruppert *et al.*, 2004). The house spider spins webs near the ceiling in corners of rooms or closet. They frequent dark less-used places such as attics, cellars barns, sheds, or under porches. The main essence of the webs is to catch prey, apart from protection and transport means. Spiders are beneficial as they catch and eat nuisance insects such as flies, ants, aphids- plant-feeding, cockroaches, small grasshoppers, crickets, leafhoppers, moths flies and mosquitoes (George and Roland, 1980). A typical web, usually built at night, has a central sheet of densely woven silk which serves as a hiding place and is anchored by numerous guy lines that are long and strong. Spiders are excellent indicators of carpenter ant infestations as their webs are commonly near the house where ants forage and become truant. While elimination of some spiders is acceptable when they are an annoyance, wholesale elimination is ecologically unsafe and results in more nuisance pests (Lanier, 1999).

Industries, street dust and motor vehicle emissions are sources of airborne particulates in urban environments (Kowalczyk *et al*., 1982; Gertler *et al.*, 2000). The presence of these particles, either airborne or as precipitated dusts poses a significant human and environmental health risk. The particles emitted by motor vehicles carry or contain heavy metals that may be toxic when present in excess of natural background levels. In general, the toxic properties of the air borne particulates are due to the biochemical activities of metals attached to them (Lighty *et al*., 2000). Spider webs act as efficient traps of airborne particulates providing a useful indicator for monitoring environmental pollutants because they are inexpensive, easy to collect and are widespread in the environment (Hose *et al.*, 2002). They are found near and around buildings and thus capture particulates to which humans may be exposed to. Spider webs have been demonstrated as effective indicators of heavy metals attributed to particulate emissions (Hose *et al.*, 2002).

In an attempt to use spider web as biosamplers, several webs were analyzed for their manganese and iron contents in both indoor and outdoor urban areas of Kano metropolis. This paper reports the levels of manganese and iron in indoor /outdoor spider webs collected from a number of sites in the urban area of Kano. The use of the spider webs can serve as a substitute for the usage of sophisticated samplers used in monitoring environmental pollution and hence give light on the extent of the environmental pollution by these heavy metals.

MATERIALS AND METHODS

Spider webs were collected from different districts in urban Kano. The areas differ in their proximities to highways and industries. Spider webs of species native to Sudan savanna eco-climatic zones (*Achaearanea tepidariorum*) were collected and analyzed for their manganese and iron contents. The webs were collected between October and April of each year; during the dry season. The samples were collected from 120 sampling sites in 10 sampling zones of Kano municipality. Each sampling zone had 12 sampling sites (Figure-1). Existing webs were removed while leaving the spider intact to rebuild the webs; spiders have the ability to quickly replace their webs when removed or damaged once they are not disturbed (Zhao, 1993; Pestproducts, 2008). The sites were marked and documented for referencing. To ensure uniform and comparable age of the webs for each site, a week old webs were harvested (Xiao-Li *et al*.; 2006). Freshly prepared webs were collected from each zone to serve as control. Once collected they were each dried and packed in clean plastic containers prior to analysis.

0.2g of each sample was digested in 70%:30% mixture of concentrated HNO_3 and hydrogen peroxide (Xiao-Li *et al.*, 2006). The digestion was completed by heating the mixture on a sand bath for about 30 minutes. The resulting solution was evaporated to almost dryness (Ruya *et al*., 2006) and redissolved in 0.1M nitric acid, transferred into 50cm^3 volumetric flasks and made to the mark with deionised water. The manganese and iron concentrations were determined by ALPA-4 model of Atomic Absorption Spectrophotometer (AAS). The result of the absorbance of each sample was the average of three sequential readings.

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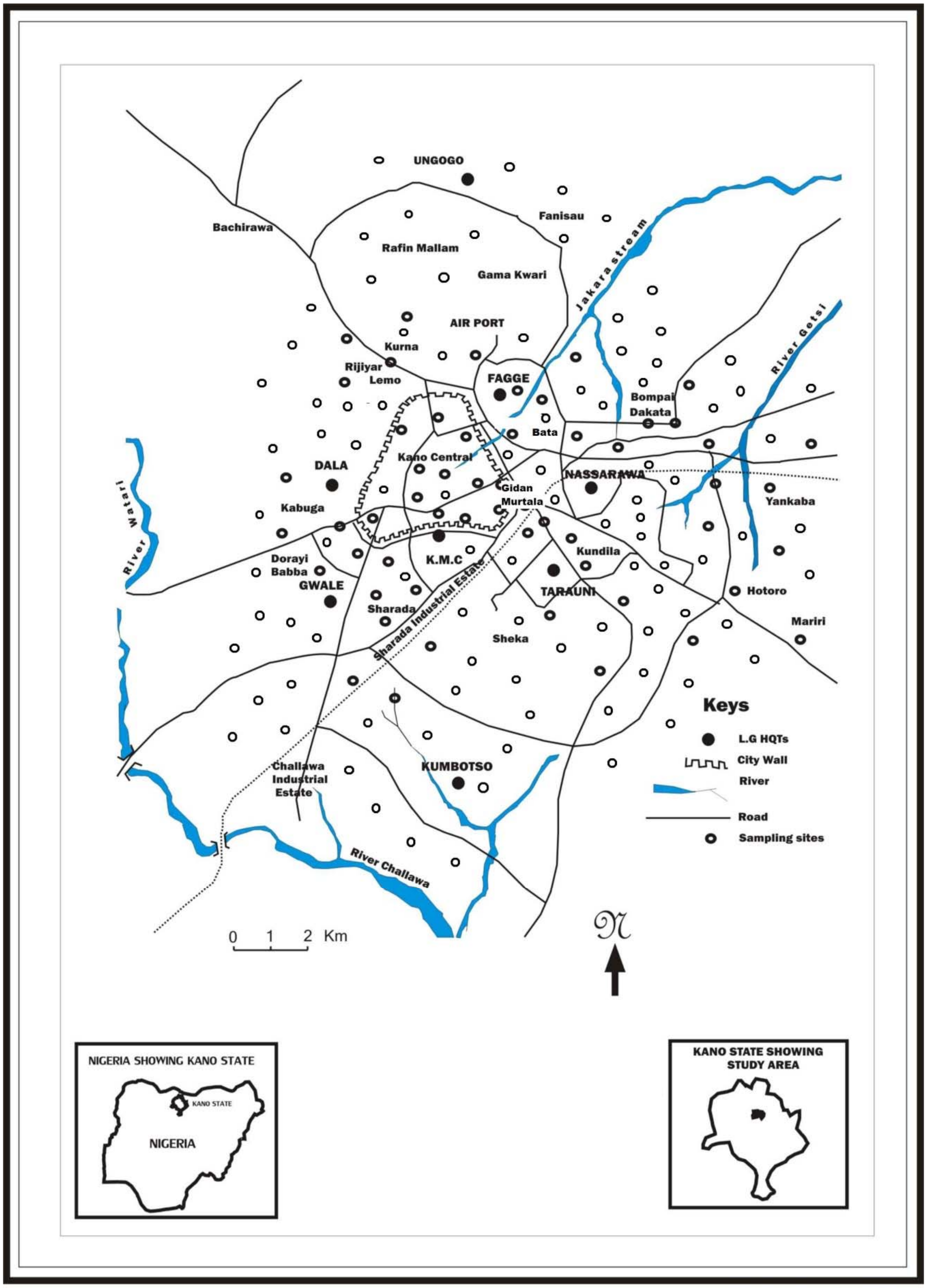

Fig. 3.1 Kano Metropolitan Map Showing Sampling Sites

Source: Geo. Dept.BUK

Figure-1. Map showing spiders webs sampling sites in Kano municipality.

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STATISTICAL ANALYSIS

The statistical analysis of the data obtained for the average indoor and outdoor manganese and iron concentrations obtained at the various sites in the municipality was carried out by using the SPSS Version 16.0 statistical software.

RESULTS AND DISCUSSIONS

The results for the analysis of the freshly constructed spider webs did not show the presence of any of the metals analysed for. This is in line with reports from other authors (Liu *et al.*, 2008; Papadopoulos *et al.*, 2009).

The indoor and outdoor frequency distribution patterns for manganese at Kano municipality are as shown in Figure-2. The indoor distribution pattern is skewed towards high frequency of low concentration with a mean of 273.33±133.98μg/g. The outdoor is normally distributed with a mean of 378.33±159.06μg/g and appearing to be higher than the indoor; showing the difference between the indoor and outdoor concentrations which might be due to the sources being more from the outside than in the buildings where there is frequent removal of the webs from the indoor than the outdoor; the outdoor webs are less disturbed than the regularly cleaned indoor. These values are comparable with those reported in other parts of the world; London (Fergusson and Ryan, 1984); New Zealand (Fergusson *et al.*, 1986); Madrid (De Miguel *et al.*, 1997), but lower than those of Oslo (De Miguel *et al.*, 1997); Hong Kong (Yeung *et al.*, 2003). The differences are most probably due to the differences in geology, industrialization and number of automobiles in the cities.

The frequency distribution patterns for iron in the Kano municipality are as shown in Figure-3. Both indoor and outdoor distribution patterns are skewed toward high frequencies of low concentrations with a mean of 3083.33±1314.00 and 4200.00±1656.00μg/g respectively. Iron has the highest concentration in the spider webs among all the metals. It is higher in the industrial, semi-industrial and high traffic zones. This shows that the sources of the metal are natural, metallurgical activities and traffic flow (Yeung *et al.*, 2003). The values obtained are lower than most of what has been reported for other cities by many workers in the world (Yeung *et al.*, 2003).

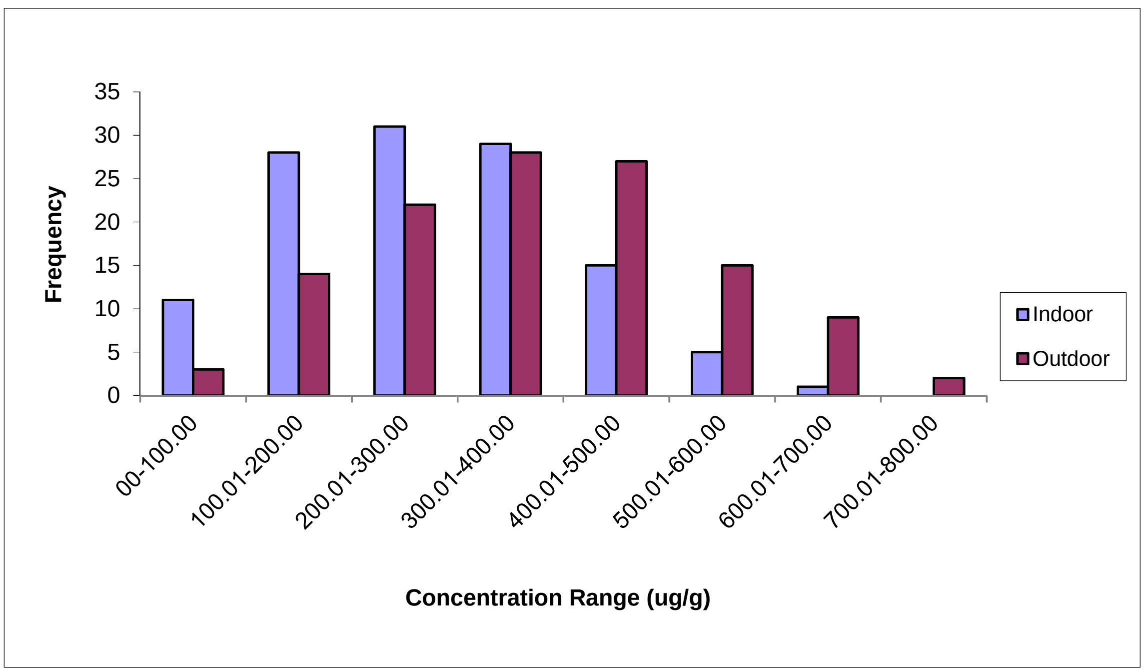

Figure-2. Frequency distribution pattern for manganese in spider webs of Kano municipality.

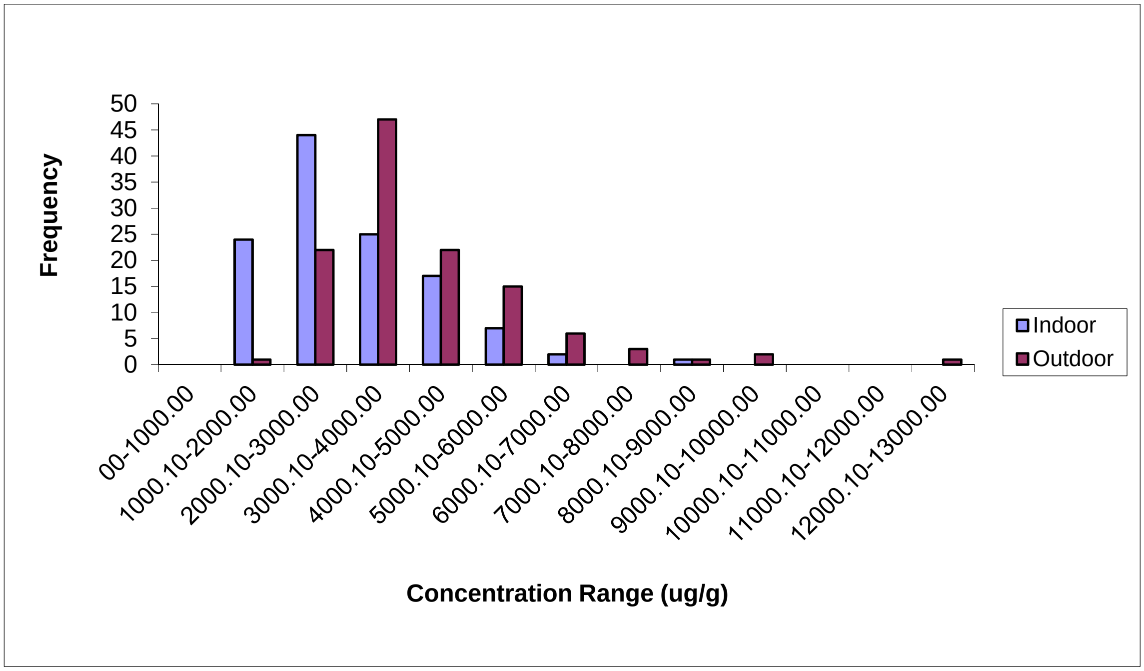

Figure-3. Frequency distribution pattern for iron in spider webs of Kano municipality.

Table-1. Parametric correlations.

		MnIndoor	MnOutdoor	FeIndoor	FeOutdoor
MnIndoor	**Pearson correlation**	**1**	**.990****	**.977****	**.944****
	Sig. (2-tailed)		**.000**	**.000**	**.000**
	N	120	120	120	120
MnOutdoor	Pearson Correlation	.990**	1	.952**	.912**
	Sig. (2-tailed)	.000		.000	.000
	N	120	120	120	120
FeIndoor	Pearson Correlation	.977**	.952**	1	.981**
	Sig. (2-tailed)	.000	.000		.000
	N	120	120	120	120
FeOutdoor	Pearson Correlation	.944**	.912**	.981**	1
	Sig. (2-tailed)	.000	.000	.000	
	N	120	120	120	120
**. Correlation is significant at the 0.01 level (2-tailed).					

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Table-2. Nonparametric correlations.

			MnIndoor	MnOutdoor	FeIndoor	FeOutdoor
Kendall's tau_b	**MnIndoor**	**Correlation coefficient**	**1.000**	**.983****	**.982****	**.983****
		Sig. (2-tailed)	.	.000	.000	.000
		N	120	120	120	120
	MnOutdoor	Correlation Coefficient	.983**	1.000	.982**	.985**
		Sig. (2-tailed)	.000	.	.000	.000
		N	120	120	120	120
	FeIndoor	Correlation Coefficient	.982**	.982**	1.000	.989**
		Sig. (2-tailed)	.000	.000	.	.000
		N	120	120	120	120
	FeOutdoor	Correlation Coefficient	.983**	.985**	.989**	1.000
		Sig. (2-tailed)	.000	.000	.000	.
		N	120	120	120	120
Spearman's rho	MnIndoor	Correlation Coefficient	1.000	.998**	.998**	.998**
		Sig. (2-tailed)	.	.000	.000	.000
		N	120	120	120	120
	MnOutdoor	Correlation Coefficient	.998**	1.000	.998**	.999**
		Sig. (2-tailed)	.000	.	.000	.000
		N	120	120	120	120
	FeIndoor	Correlation Coefficient	.998**	.998**	1.000	.999**
		Sig. (2-tailed)	.000	.000	.	.000
		N	120	120	120	120
	FeOutdoor	Correlation Coefficient	.998**	.999**	.999**	1.000
		Sig. (2-tailed)	.000	.000	.000	.
		N	120	120	120	120
**. Correlation is significant at the 0.01 level (2-tailed).						

The multivariate analysis technique, analysis of variance through ANOVA, t-test, Pearson's parametric correlation (Table-1), Kendall's tau_b and Spearman's rho nonparametric correlation (Table-2) analyses were applied. The considered variables were the normalised concentrations of Mn and Fe determined in indoor and outdoor concentrations. When comparing the indoor and the outdoor distribution the latter appeared superior in accumulating higher amounts of the metals because of its ready availability to trap the dust particles laden with the metals since most of the sources are outdoor ones. For all the concentrations of the two metals in the sampling zones the indoor and outdoor are significantly correlated ($P<0.01$).

African countries have the worst record for suspended particulate matter in rural homes, while Latin America, India and China are the worst for suspended particulate matter in urban interiors (Bascom, 1996; Albalak *et al*., 1999; Naeher *et al*., 2000). Although most monitoring is being carried out on ambient (outdoor) air,

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whereas many health problems potentially linked to indoor air pollution still go unrecognized. For example several studies have shown that coal smoke has a strong risk factor for lung cancer among non-smoking women, while another study has related lung cancer to the past use of bio-fuels in cooking (Ellegard, 1996; Zhang and Smith, 1996).

CONCLUSIONS

Since the results for the analysis of the freshly constructed spider webs did not show the presence of any of the metals analysed for. Thus is a confirmation that these metals did not originate from the spider silk and therefore the metals were inputs from the environment.

The concentration of the two metals in the spider webs is a function of their proximity to major highways, industrial areas and types of activities in the immediate surroundings. The results obtained exhibit a range of concentrations between the industrial, residential and commercial areas. Therefore the primary sources of these metals in spider webs are re-suspension of soil derived dust, automobile exhausts, geochemical processes, and windblown dusts. From the results automobile sources appeared to be the major ones. In urban cities, people are exposed to a variety of potentially toxic chemicals. Of particular concern is the inhalation of fine-grained atmospheric particles with high concentrations of heavy metals. From the data obtained in the urban areas of Kano, significant anomalies were detected and some conclusions could be drawn that in urban cities, people are exposed to a variety of potentially toxic chemicals. This analysis has also proved that spider webs can be used as indicators of the pollutants of the environment from which they were collected and that spider webs being natural device for sample collection can even be more efficient than many other devices as collection is continuous 24 hours a day and they are very common, and chief.

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