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# Spider Webs as Indicators of Heavy Metal Pollution in Air

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Motor vehicle emissions are a major source 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 (e.g. Cu, Zn, Cd, Pb) that may be toxic when present in excess of natural levels. Indeed, the toxic properties of airborne particles may be due in part to the biochemical activity of metals attached to them (e.g. Smith and Aust 1997; Lighty et al. 2000). It is critical to monitor particulate emissions in roadside environments to assess potential human and environmental health risks, and implement control measures when necessary.

Spiderwebs are efficient traps of airborne particulates and provide a useful indicator for monitoring environmental pollutants because they are inexpensive and easy to collect, and are widespread in urban areas (Hose et al. 2002). They also occur in and around buildings and thus capture particulates to which humans are exposed. Hose et al. (2002) demonstrated that spiderwebs were effective indicators of heavy metals attributed to motor vehicle emissions. Analyses of the webs also reflected the geology and biology of the cave environments from which they were collected.

In this study we test the suitability of spiderwebs as indicators of motor vehicle emissions in urban environments. Because of the many sources of heavy metals and particulates in urban environments, it is important that webs are able to detect heavy metal pollution from motor vehicles beyond potentially high background concentrations. We analysed the webs of two commonly occurring spiders, *Achaearanea tepidariorum* (C.L. Koch 1841) (Araneae: Theridiidae) and *Araneus ventricosus* (L. Koch 1878) (Araneae: Araneidae), for Pb, Zn, Cu and Cd from urban sites in Wuhan, Hubei province, China. The aim of this study was to compare the concentrations of these heavy metals in the webs and determine whether there was a relationship between metal concentrations and the proximity and volume of motor vehicle traffic at the sites. We also explored the effect of web age on metal accumulation, and compared the accumulation of metals in webs of the two species.

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## MATERIALS AND METHODS

Spider webs were collected from two urban areas, Dohu and Shahu, in Wuhan, Hubei province, China. The distance between the sites is approximately 5 km. The sites have similar climatic and geologic characteristics, but differ in their proximity to motor vehicle traffic. The Dohu site is adjacent to a heavy traffic road that carries approximately 12000 vehicles per day. Within the Dohu site we had two sampling areas, Dohu area A (hereafter DHA) which was 10-20 m from the road, and Dohu area B (hereafter DHB) which was 70-80 m from the road. The Shahu site is located over 1 km from the nearest road (which carries only light traffic) and is approximately 3 km to the nearest major road that carries 4000 vehicles per day. Contamination from motor vehicles is generally limited to a strip within 100 m of the roadway, although fine particulate emissions may be carried further afield, and combined with airborne particulates from other urban and industrial processes contribute to the background contamination expected in urban environments. The Shahu site (hereafter SH) represents an urban reference site because it is remote from major roads and major point sources. Webs collected from this site reflect the background contamination in the urban environment.

We collected and analysed the webs of two species: *Achaearanea tepidariorum* and *Araneus ventricosus. Achaearanea tepidariorum* is native to South America but through introduction is now distributed globally. This spider constructs frame webs that consist of a loose sheet that is attached to a substrate with sticky threads that catch prey (Foelix 1982). The spider often builds its web indoors or around houses and other buildings. These webs can persist for over a year, but the spider will build new webs if previous webs are removed or badly damaged (Zhao 1993).

*Araneus ventricosus* is common across north and south of China. The spider constructs a regular and (usually) vertical orb web that consists of 15-22 radial and structural threads and a spiral of 10-15 sticky catching threads. Unlike other members of the genus, *A. ventricosus* does not ingest and rebuild its web daily. Instead, webs last for 7-10 days. Orb webs may be easily damaged by wind, rain or early morning dew, in which case they may be mended by the application of additional silk. Webs are found on trees and a variety of built structures.

To determine whether spider webs can indicate motor vehicle pollutants above the urban background levels, and whether there were differences among species, we compared the metal concentrations in new webs of both species collected from DHA and our reference site SH. To determine whether proximity to traffic affects the accumulation of metals, we compared new *A. ventricosus* webs from DHA and DHB. To determine whether web age affects the accumulation of metals, we compared existing and newly constructed *A. tepidariorum* webs collected from DHA.

Webs of both species were collected between March 2004 and May 2005. To ensure the age of webs collected was comparable for each species and at each site, we used newly constructed webs for most comparisons. To collect newly constructed webs, webs containing spiders were located and the locations closely documented. Existing webs were removed while leaving the spider intact to rebuild a new web. We returned to the same location 7 days later to remove the newly constructed web. Once collected, webs were placed in a clean vial and frozen for later analysis. We also retained the original/existing webs of *A. tepidorium* for comparison with the newly constructed webs.

Frozen web samples were thawed and dried for 48 h at 70°C, and then weighed on a Mettler AT 21 Comparator balance to nearest 0.01 mg. Subsequently, webs were digested in a 70%:30% mixture of concentrated ultra-pure nitric acid (70%) and hydrogen peroxide. The digestion was completed with the microwave destruction procedure described by De Wit et al. (1998). Samples were diluted to 25 ml with de-ionized water and stored at -20°C until required for analysis. Metal concentrations were determined by flame atomic absorption spectrometry (SpectrAA-10; Varian, Palo Alto, CA) for Zn and Cu and on a graphite furnace AAS (SpectrAA-100), equipped with Zeeman correction for Pb and Cd. Average recoveries in spiked samples were 102.1%, 98.4%, 95.8% and 96.3% for Pb, Zn, Cu, and Cd, respectively. Prior to analysis, all glassware was washed and soaked for 48h in a 10% (1.67 M) nitric acid solution, triple rinsed in distilled de-ionized water and air-dried.

To support our classification of reference and test sites, we also compared the volume of airborne particles at each site. Levels of airborne particulates were compared by measuring the total suspended particulates (TSP) in the air using a Wuhan Tianlian TSP sampler (model CH-5C02) with a pumping rate of 60 L/min. The sampler was placed at a height of 1.5 m and operated for 5 minutes at 7:00, 9:00, 10:00, 13:00, 15:00 and 17:00 on random days during the study. Measurements were made simultaneously at both sites. The sampler filters air through a 1-μm filter that was dried and weighed before and after sampling to determine the mass of dust collected. The mass of dust collected was divided by the volume of air sampled (300 L) to determine the TSP concentration.

Data were analysed using students t-tests (Winer et al. 1991). The significance level (α) for all tests was 0.05.

## RESULTS AND DISCUSSION

The concentrations of Pb, Zn, Cu and Cd in new *A. tepidariorum* webs were significantly greater ($P<0.05$) at DHA than SH. The difference between the two sites was greatest for Pb; the mean Pb concentration in webs from DHA was approximately 6 times higher than in webs from SH (Table 1). Pb, Zn, Cu and Cd levels in *A. ventricosus* webs were also significantly higher ($P<0.05$) at DHA than at SH. As for *A. tepidariorum,* the differences between the two sites were greatest for Pb; the mean Pb concentration at DHA was approximately 4.5 times higher than at SH (Table 1).

**Table 1.** Average concentration (±SD) of metals in newly constructed webs of *A. tepidariorum* and *A. ventricosus,* and total suspended particulates (TSP) from Dohu site A (DHA), Dohu site B (DHB) and Shahu (SH). Metal concentrations expressed as μg/g dry weight. TSP concentrations expressed as μg/m$^3$.

| | n | DHA | DHB | SH |
|---|---|---|---|---|
| *A. tepidariorum* | | | | |
| Pb | 7 | 289.74 ± 134.02 | - | 48.44 ± 31.01 |
| Zn | 7 | 647.64 ± 280.79 | - | 261.91 ± 81.59 |
| Cu | 4 | 17.35 ± 4.14 | - | 7.03 ± 1.85 |
| Cd | 4 | 3.37 ± 0.85 | - | 1.69 ± 0.49 |
| *A. ventricosus* | | | | |
| Pb | 7 | 162.87 ± 89.19 | 78.61 ± 43.07 | 35.42 ± 14.36 |
| Zn | 7 | 371.41 ± 68.13 | 250.41 ± 77.10 | 150.20 ± 36.91 |
| Cu | 4 | 12.38 ± 4.79 | 8.37 ± 2.69 | 5.19 ± 1.44 |
| Cd | 4 | 2.71 ± 0.12 | 1.61 ± 0.59 | 0.85 ± 0.36 |
| TSP | 14 | 426 ± 193 | - | 284 ± 108 |

Determining the exact source of the metals in the webs is beyond the scope of this study, however, particulate emissions from motor vehicles are a probable source. Pb, Zn, Cd and Cu are common elements in the particulate emissions from motor traffic (De Miguel et al. 1997; Sternbeck et al. 2002). With the removal of lead from most petrol worldwide, combustion of fuels is now an insignificant source of Pb emissions, but may contribute Zn and Cd (Sternbeck et al. 2002). Brake linings are now the most common source of Pb in roadside environments, although resuspension of lead contaminated dusts remains an issue (De Miguel et al. 1997). Wear of brake linings is the principal source of Cu, and the wear of tyres and motor oils are considered the primary sources of Zn (Sternbeck et al. 2002). The TSP sampling showed that DH had significantly greater ($P<0.05$) concentrations of airborne particulates than SH (Table 1), which is consistent with our assumption that the metals in webs are derived from particulate vehicle emissions.

Our results indicate a reasonably high level of metals in webs from our urban reference site, SH, which can be attributed to the smaller, more mobile particulate emissions, and those from other diffuse urban and industrial sources. The concentrations of lead and zinc in SH webs were considerably greater than those reported in webs from reference sites by Hose et al. (2002). Hose et al. (2002) collected webs from reference sites that were more than 30 km from the nearest major road or urban area. Those webs contained around 100 μg Zn/g and 30 μg Pb/g, which are much less than the concentrations recorded in our urban reference site. Notwithstanding differences in web age and species, the comparison to Hose et al. (2002) suggests a high background level of metal concentrations in urban areas.

Just as metal concentrations varied between SH and DHA, which differed in the distance to major roads, so too there were significant differences in the concentrations of metals between DHA and DHB. The concentrations of Pb, Zn and Cd in new *A. ventricosus* webs from DHA were significantly higher ($P<0.05$) than in webs from DHB, which was a further 50 m from the road. However, the concentrations of Cu were not significantly different ($P >0.05$) between DHA and DHB (Table 3). These findings for Pb, Zn and Cd are consistent with past studies that have shown a decrease in metal concentrations with increasing distance from the road (e.g. Yassoglou et al. 1987). This may be explained by De Nevers (1999) who showed that about 40% of particulate vehicle emissions have diameters larger than 9 µm that, because of their high gravitational settling velocity, settle quickly and are deposited within about 10 m of the road. About 20% of the particles have diameters between 1 and 9 µm and are deposited within about 40 m of 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 from the road.

The lack of significant differences for Cu suggests either 1) that this metal is mainly associated with small particulates that may be distributed evenly over DH, or 2) an issue of statistical power. 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). According to De Nevers (1999), particles of this size should precipitate within about 40 m of the road, leading to a significant difference between DHA and DHB, and thus suggesting insufficient power in our statistical analysis. Future studies of this nature should have >4 replicates to avoid such problems.

Old *A. tepidariorum* webs collected from DHA had significantly greater ($P<0.05$) concentrations of Pb, Zn, Cu and Cd than newly constructed webs (Table 2), suggesting that the longer the webs persist in the environment, the greater are the heavy metal loads they accumulate. This also highlights the importance of knowing web age when sampling for air quality assessment. Because webs accumulate metals over time, they provide an integrated assessment of contamination at a site, which gives webs a distinct advantage over conventional air sampling strategies (such as dynamometric tests) that only provide a snapshot of conditions. Future research should explore further the rates of accumulation of metals in the webs. Our research has been an important first step in this regard. Future research should also relate metal concentrations measured in webs to airborne concentrations to establish a direct link between web loads and human health risks.

**Table 2.** Average concentration (±SD) of metals in newly constructed (new) and existing (old) webs of *A. tepidariorum* Dohu site A (DHA). Concentrations expressed as µg/g dry weight.

| Metal | n | New webs | Old webs |
|---|---|---|---|
| Pb | 7 | 289.74 ± 134.02 | 793.60 ± 195.14 |
| Zn | 7 | 647.64 ± 280.79 | 1451.29 ± 309.97 |
| Cu | 4 | 17.35 ± 4.14 | 34.68 ± 8.06 |
| Cd | 4 | 3.37 ± 0.85 | 10.92 ± 3.78 |

Concentrations of metals were consistently higher in *A. tepidariorum* than *A. ventricosus,* which is a likely consequence of web structure and design. *A. ventricosus* webs are short lived and are rebuilt every 7 to 10 days. The web is a vertically arranged orb that relies on passing airborne particles adhering to the webs many sticky catching threads. Sticky threads such as these require regular renewal to maintain their function (Foelix 1982). *A. ventricosus* web is also built in open and exposed areas to catch flying prey, which makes it prone to damage, hence the need for frequent repair and renewal. Normally, *A. ventricosus* will digest its old web before constructing a new one, which provides a high likelihood that the spider is ingesting the heavy metals on the web and enabling those metals to enter the food web. In contrast, *A. tepidariorum* builds messy horizontal sheets that are effective traps for settling dust. These webs can persist for over a year and may thus be suitable for monitoring over long periods. *A. tepidariorum* web contains relatively few sticky catching threads and hence does not require such a high level of maintenance and replacement. These features suggest that *A. tepidariorum* web is better able to accumulate airborne particles of heavy metals, and therefore would be a more effective species in environmental monitoring of heavy metals, particularly of long-term changes in polluted sites.

In this study we have shown that spider webs are effective indicators of heavy metals associated with motor vehicle traffic in urban areas. We found significant differences in the heavy metal concentrations in spider webs between the polluted and reference site, which we attribute to differences in the volume and proximity of road traffic. We also found age- and distance-related differences in metal levels in spider webs. Further research is required to establish a quantitative relationship between levels of pollution in the environment and those measured in the webs.

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