HEAVY METAL CONTENT IN THE BARK OF CAMPHORA TREE IN XIANGTAN AND ITS ENVIRONMENTAL SIGNIFICANCE

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Abstract. With rapid economic development, Xiangtan, as an old industrial base of China and a famous industrial city in Hunan Province, caused severe pollution, which had a significant impact on people's lives. To understand the heavy metal pollution in Xiangtan, we tested and analyzed the barks of *Cinnamomum camphora* in different functional areas. The article examined the differences and sources of heavy metal contents in the bark of *Cinnamomum camphora* from different functional areas. The results showed that the contents of various heavy metals in the barks of *Cinnamomum camphora* varied considerably and the most common elements of heavy metal pollution were Mn, Pb, and Cr. The activities in different functional areas had a significant influence on the enrichment of heavy metals in the bark of *Cinnamomum camphora*. Heavy metals in the business district mainly came from traffic emissions and various domestic wastes. High population density and household litter affected the heavy metal contents in the Residential District. Heavy metal contents were high in parts of the urban green space due to living garbage or surrounding environment.
Keywords: *pollution, functional areas, spatial distribution, bark, indicator*

Introduction

With the rapid development of the global economy, pollutants containing various heavy metals enter the environment in different ways. Heavy metal pollution can gradually become a serious environmental issue. The hazards of heavy metals including both existing and potential forms have an almost irreversible effect on ecosystems and human health (Sun et al., 2011; Zhang et al., 2012, 1998). Heavy metal pollution has many characteristics, including latency, cumulativeness, long lifespan, and irreversibility. If we do not take immediate and effective measures, it will have a more severe impact. Heavy metals in the environment mainly come from gas emissions, road traffic emissions and industrial emissions (Yao et al., 2012; Zhang et al., 2012). Previous studies showed that heavy metals in plant surface often decreased with increasing distance from pollution sources (Zhu et al., 2007; Chen et al., 2016).

There are various methods to detect atmospheric heavy metal pollution. Broad-leaved and coniferous trees, such as mosses, lichens, vascular plants, and woody-plants, can be utilized to study air pollution (Sun et al., 2011; Huang et al., 1983, 1984; Fang et al., 2000). Because the surface layer of plant contacts more with the atmosphere and is sensitive to environmental changes, it becomes a significant carrier for monitoring air pollution. Though barks do not absorb heavy metals and other pollutants sensitively as mosses do, it is a good indicator of other contaminants, such as electrical conductivity, pH, sulfur, nitrogen, heavy metals, and so on (El-Hasan et al., 2003). Because

Cinnamomum camphora is a street tree and its bark is exposed to the atmosphere for a long time, it has a large contact area with the atmosphere. Barks of *Cinnamomum camphora* not only contained heavy metal elements absorbed from the soil but also accumulated a large amount of dust and particles from the atmosphere (Huang et al., 1983; Zhou et al., 2014). Therefore, this paper chose barks of *Cinnamomum camphora* as an indicator of air pollution to study.

Xiangtan is an old industrial city. In recent years, with the continuous development of industry and economy, the heavy metal contents of Xiangtan have increased sharply. This study tries to analyze the spatial distribution characteristics of heavy metal in the barks of *Cinnamomum camphora* in Xiangtan, reveal the sources and causes of heavy metal pollution, and explore the pollution situation. This study can not only investigate the causes and extent of heavy metal pollution in Xiangtan City but also provide a scientific basis for ecological research in urban areas. It is also helpful to environmental governance, human health, urban eco-environment, and sustainable urban development.

Materials and methods

Research area

Xiangtan City (111°58'E-113°05'E, 27°21'N-28°05'N) is a prefecture-level city in the east-central of Hunan Province, with a total area of 5015 km^2. It is the smallest prefecture-level city in Hunan Province, China. In 2010, the city's resident population was 2.748 million, of which 959,000 were in the urban area, with a population density of 549 people/km^2, ranking second in Hunan Province. The climate of Xiangtan belongs to a subtropical monsoon humid climate with abundant precipitation, sufficient solar and thermal resources. Although the annual rainfall reached 1200-1500 mm, the time distribution was uneven, and the inter-annual variability was considerable (Xiao, 1996).

Xiangtan's geographical position is superior. Many expressways and railways meet and pass here, which is highly beneficial to the economic development of Xiangtan. Simultaneously, Xiangtan, together with Changsha and Zhuzhou, is the "Golden Triangle" urban agglomeration with the most developed politics, economy and culture in Hunan Province (Xiao, 1996). In recent years, Xiangtan's economy has been growing, especially in various industries. Xiangtan has grown up to be a heavy industrial city with mechanical, metallurgical, chemical and textile industries. Main industrial types include coal, metallurgy, chemical fiber, chemical industry, textile, leather, agricultural products' processing, etc. Among them, industrial products with national influence are iron and steel, military products, electromechanical products, and some chemical products.

Sampling and analysis

In January, 2015, the barks of *Cinnamomum camphora* in different functional areas, such as the Residential District (Shuxiangyulin, near the railway station), Commercial District (Bus Station), Industrial District (Xiangtan Iron & Steel Co. Ltd of Hunan Valin, Longpai Food Limited by Share Co. Ltd) and Urban Green District (Baishi Park, Yuhu Park, Yuetang Park, Peace Park), were sampled (*Fig. 1*). The barks of 3-5 selected *Cinnamomum camphora* trees, which have similar age and a 25-45 cm diameter at breast height in one place, were taken from the same side of the trunk at 1.3-1.5 m above the ground surface.

When sampling, the adhesives on the bark's surface were removed with a hard brush, then the barks of 5×5 cm^2 were scrape off with a stainless steel knife. To prevent contact pollution and increase the experiment error, polish the bark's surface with sandpaper. The samples were enclosed in a polyethylene self-sealing bag and numbered. Synchronously, the sampling point, sampling time, weather condition, geographical location, altitude and tree height, etc were recorded.
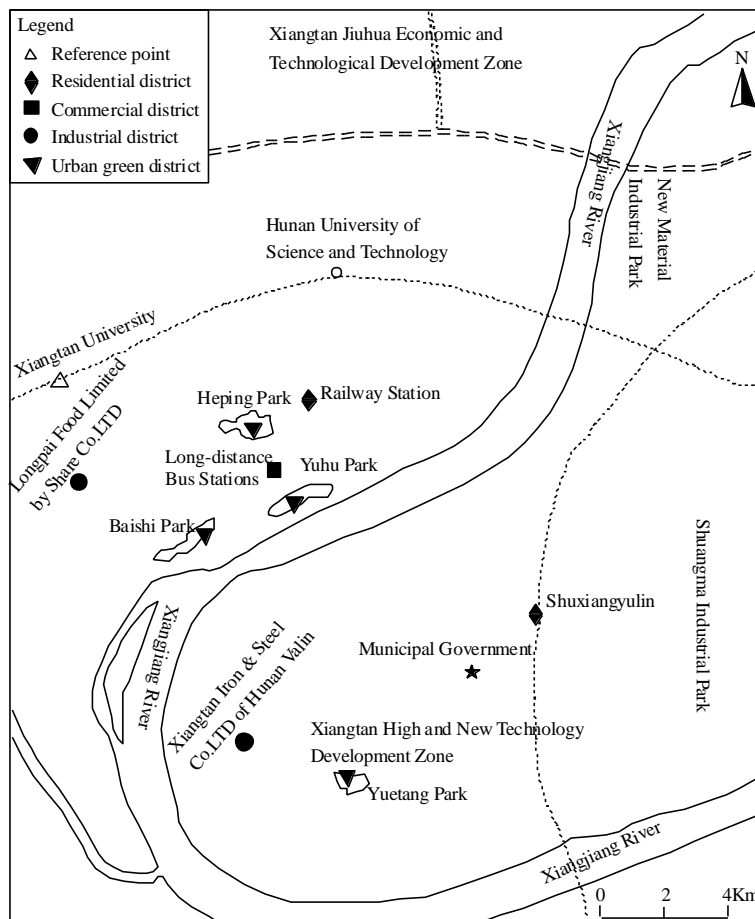

Figure 1. Schematic diagram of sampling sites

In the laboratory, the impurities were removed and the samples were baked to a constant weight at 105 °C in a thermostat. Then, the dried sample was ground in an agate mortar through a 100 mesh nylon sieve. Next, 2 ml HCL, 5 ml HNO$_3$ and 2 ml H$_2$O$_2$ were added to 0.5 g ground samples that were digested by microwave digestion (Zhuang et al., 2000). Afterward, the digested samples were heated at 300 °C for 4 h by an electric heating plate to remove the acid. After sample treatment, a FAAS (flame atomic absorption spectrophotometer) was utilized to test the content of heavy metal (Cd, Pb, Cr, Cu, Mn) (Lü, 2008; Sharifi et al., 2017; Kord et al., 2010; Ahmad Afif, 2010; Xie et al., 2009). The correlation between the standard solution was at least 0.99, the error of the heavy metal content of the parallel sample was less than 5%, and every five groups added a blank sample. All experimental data must be subtracted from the blank sample to ensure accuracy.

Results and analysis

Heavy metal contents in the bark of Cinnamomum camphora

Because Xiangtan University is located in the suburb of Xiangtan City, we take the heavy metal contents in the barks of *Cinnamomum camphora* at Xiangtan University as preset reference values to reveal the regional differences due to its good environmental conditions (*Fig. 2*).
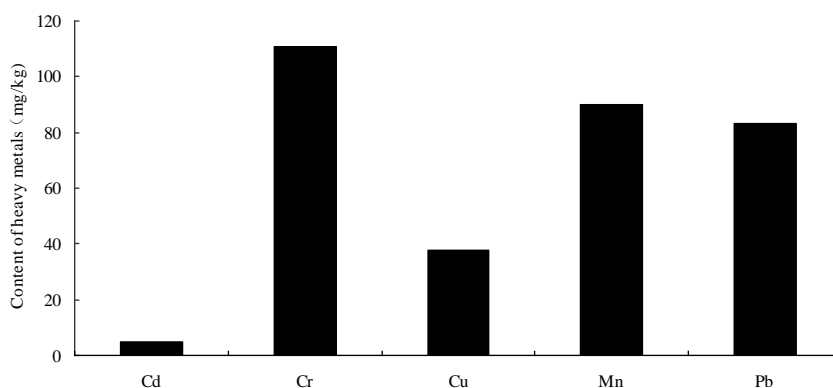

Figure 2. Contents of heavy metals in the bark of Cinnamomum camphora at Xiangtan University

The average content of Cd in Xiangtan is 5.35 mg/kg, with a range of 2-10.0 mg/kg; Average content of Cr is 117.35 mg/kg, with a range of 42.0-266.0 mg/kg; Average content of Cu is 44.376 mg/kg, with a range of 23.74-126.42 mg/kg; Average content of Mn is 304.529 mg/kg, with a range of 19.5-1214.56 mg/kg; Average content of Cr is 86.65 mg/kg, with a range of 30.0-220.0 mg/kg (*Tables 1* and *2*). Average heavy metal content in the barks of *Cinnamomum camphora* was Mn > Cr > Pb > Cu > Cd, and the content of Mn reached 304.529 mg/kg. The content of Mn in Xiangtan has a high background value, which is a factor with local characteristics. The above situation may be related to the long-term mining of Mn in Xiangtan Manganese Mine. During over 100 years of mining, tailing, slag and sewage were not treated effectively and timely, resulting in the loss and diffusion of Mn. Manganese can diffuse into the atmosphere and soil through a variety of approaches (Xie et al., 2005; Xi et al., 2008). Plants can absorb manganese through their roots, accepting atmospheric deposition, and absorption function of plants themselves, so that the manganese content in plants reached a higher level.

Heavy metal contents in the barks of Cinnamomum camphora in different functional districts and their sources

Content and spatial distribution of heavy metals in the barks of *Cinnamomum camphora* were different in different functional regions in Xiangtan city (*Table 2*). The content of the heavy metals in each functional district is Industrial Area > residential area > urban green area > commercial area. Among them, the heavy metal content in the Industrial District was the highest, and the maximum value reached 1301.5 mg/kg. The highest content of manganese also appeared in the Industrial District, reaching

736.68 mg/kg. The maximum heavy metal contents in the Residential District reached 947.06 mg/kg, and the contents of Mn, Cr, and Pb were relatively high. Urban Green Districts in this research were mainly urban parks, and their environments are relatively good. Overall, the heavy metal content of the barks of *Cinnamomum camphora* in Urban Green Districts is lower than that in industrial and Residential Districts. However, because Yuetang Park is located close to the old industrial zone of Xiangtan Iron & Steel Co. Ltd of Hunan Valin, environmental pollution around Yuetang Park was severe, and the maximum heavy metal content reached 833.42 mg/kg.

Table 1. *Heavy metal contents in Cinnamomum camphora in Xiangtan (mg/kg)*

Heavy metal	Cd	Cr	Cu	Mn	Pb
Average	5.35	117.35	44.376	304.529	86.65
Range	2.0-10.0	42.0-266.0	23.74-126.42	19.5-1214.56	30.0-220.0
Standard deviation	1.994	51.089	19.242	261.859	42.944

Table 2. *Fundamental characteristics of heavy metal in the barks of Cinnamomum camphora in different functional districts (mg/kg)*

Functional district		Cd	Cr	Cu	Mn	Pb	Total
Residential district	Maximum	8	124	43.82	653.24	118	947.06
	Minimum	4	46	29.16	77.08	60	216.24
	Average	5.3	104	33.66	318.78	79.67	541.41
Commercial district	Maximum	6	162	126.42	222.94	104	621.36
	Minimum	4	78	39.18	84.36	30	235.54
	Average	4.33	113.67	65.81	161.82	59.67	405.3
Industrial district	Maximum	10	266	68.52	736.68	220	1301.2
	Minimum	4	78	39.96	169.14	92	383.1
	Average	6.5	164.25	53.37	405.33	133.75	763.2
Urban green district	Maximum	10	150	65.44	330.86	144	700.3
	Minimum	2	42	23.74	115.36	32	215.1
	Average	5.29	94.57	37.92	221.73	67.57	427.08
Reference point	Maximum	6	150	37.64	149.5	182	525.14
	Minimum	4	106	35.32	69.16	52	266.48
	Average	5	125	36.74	126.68	102.33	395.75

The sources of heavy metal pollution in cities are exceptionally incredible, and the primary pollution sources in diverse functional areas are different. The highest heavy metal content in the barks of *Cinnamomum camphora* in Xiangtan is Mn due to the exploitation of Xiangtan Manganese Mine. However, the content of manganese is different in various functional areas (*Table 3; Fig. 3*). The manganese content in Shuxianglin was 333.96 mg/kg, ranking third in all sampling sites. Besides Mn, the content of Cr and Pb was relatively high, reaching 160 mg/kg and 78 mg/kg respectively. The dense buildings, less greening area, a large population density, large living garbage, living sewage and a large amount of exhaust gas from the combustion of domestic fuel near this district led to the high content of Mn, Cr, and Pb. Besides,

Shuxiangyulin Community is next to Ji'an Road and not far away from the Xiangtan East Automobile Station. Barks of *Cinnamomum camphora* might accumulate a large amount of automobile exhaust and road dust due to the huge traffic flow, which may also be the reason for the high content of Cr and Pb. The minimum values of Cr and Mn appeared near the Railway Station, reaching 68 mg/kg and 78.12 mg/kg. The principal reasons are its location close to the suburbs, the low buildings and the small traffic flow of the adjacent roads.

Table 3. Heavy metal content in different sampling areas of different functional districts (mg/kg)

| Functional district	Site	Cd	Cr	Cu	Mn	Pb	Total
Residential district	Shuxiangyulin	5	160	31.08	333.96	78	608.04
	Near the railway station	4	68	30.7	78.12	67	247.82
Commercial district	Bus station	5	137	48.83	214.83	92	497.66
Industrial district	Longpai Food Limited by Share Co. Ltd	6	210	39.96	233.28	114	603.24
	Xiangtan Iron & Steel Co. Ltd of Hunan Valin	8	79	62.34	712.89	202	1064.23
Urban green district	Baishi Park	3	101	32.62	127.08	71	334.7
	Yuhu Park	8	54	29.15	119.67	59	269.82
	Yuetang Park	6	82	34.94	304.48	77	504.42
	Peace Park	4	68	33.79	168.82	43	317.61
Reference site	Xiangtan University	5	111	37.64	89.85	83	326.49
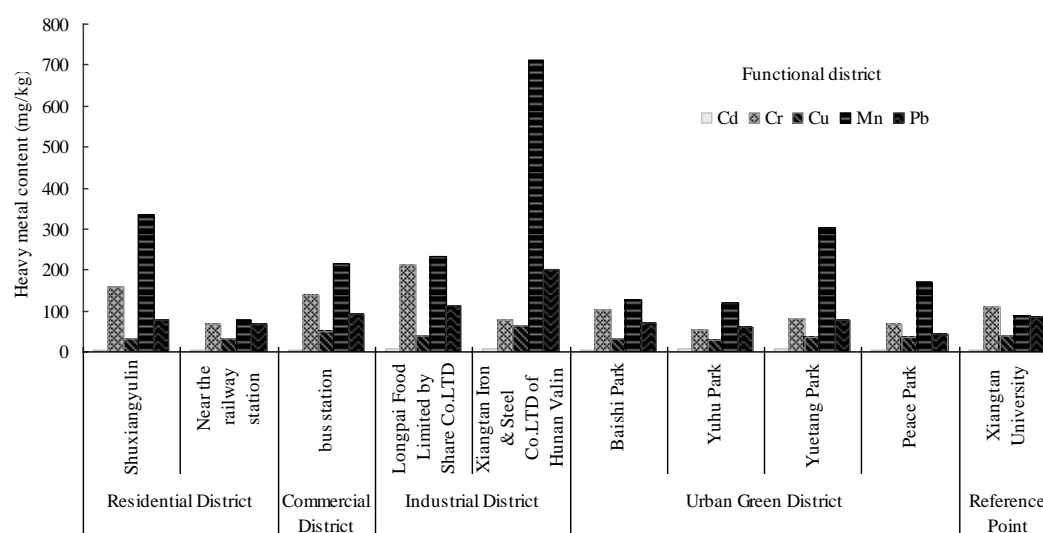
Figure 3. Contents of heavy metals in the barks of Cinnamomum camphora in different functional areas

The contents of Cd, Cr, Cu, Mn and Pb in the barks of *Cinnamomum camphora* were high in the Commercial District. The Long-distance Bus Station, as an essential part of the Commercial District, is located in the centre of Xiangtan City and has various food,

accommodation and entertainment industries, resulting in more garbage compared to other areas. Moreover, a large number of heavy metals can be produced by exhaust emissions from vehicle fuel combustion and dust in this district because of the massive traffic volume. These heavy metals will enter the atmosphere, and then accumulate on the surface of the barks of *Cinnamomum camphora* through atmospheric sedimentation and plant adsorption.

In the Industrial District, the heavy metal contents in the barks of *Cinnamomum camphora* are very high (*Tables 2* and *3; Fig. 3*). The maximum value of Mn and Pb both found in Xiangtan Iron & Steel Co. Ltd of Hunan Valin (*Fig. 3*) and reached 712.89 mg/kg, 7.9 times that of the reference point. The content of Pb reached 202 mg/kg, 2.4 times that of the reference point. The main reason why the heavy metal content of Xiangtan Iron & Steel Co. Ltd is so high is that it is a long-standing iron and steel enterprise with a complete set of technological processes, such as coking, sintering, ironmaking, steelmaking, rolled materials and so on. A large number of waste gas, wastewater, and residues containing Mn, Pb, Cd, and other heavy metals can discharge during the production process, and then enter the atmosphere and soil. After atmospheric deposition and rain wash, the heavy metal would accumulate in plants by absorption and adsorption through roots and barks. Therefore, the heavy metal contents in the barks of *Cinnamomum camphora* were high. At Longpai Food Limited by Share Co. Ltd, due to small greening, dense buildings and large traffic volume, the contents of Cr, Mn, Pb, and other heavy metals in the barks of *Cinnamomum camphora* are also relatively high, reaching 210 mg/kg, 233.28 mg/kg and 114 mg/kg, respectively.

Although Yuetang Park is an urban green space, it is located in the old industrial area and has a long history. Besides, it is close to Xiangtan Iron & Steel Co. Ltd, a critical pollutant enterprise. Therefore, the content of Mn in the barks of *Cinnamomum camphora* in this area even reaches a high level of 304.48 mg/kg, which is the place where the maximum content of Mn and Pb appears in urban green space. From *Table 3*, the highest content of Cr appears in Baishi Park, and the content is 101 mg/kg. Baishi Park lies in the old city centre of Xiangtan. There are more residents around it, and the traffic flow near the sampling point is also significant. Similar to other places with the high contents of heavy metal, road dust and living sewage are the main reasons for the high content of Cr in this area.

Conclusion

Heavy metal contents in the barks of *Cinnamomum camphora* had a specific accumulation and could indicate the air pollution condition in Xiangtan. The results showed that:

- The contents of Cr, Mn, and Pb in the barks of *Cinnamomum camphora* were the highest. Among them, the content of Mn exceeded seriously, and the average content was Industrial District > Residential District > Urban Green District > Commercial District. The maximum value of Mn appeared at Xiangtan Iron and Steel Co., with a high value of 712.89 mg/kg, which was 7.9 times the reference point.
- Heavy metals in the barks of *Cinnamomum camphora* mainly were produced by traffic discharge, living waste, manganese mining, and industrial enterprise discharge. The heavy metal contents in the barks of *Cinnamomum camphora* in the industrial area and its adjacent urban green space was high, which was

mainly due to the production and emission of industrial enterprises. For Commercial Districts, the high contents of heavy metal were affected primarily by the traffic flow, automobile exhaust, and domestic waste. Population density and domestic waste were the significant factors affecting the heavy metal in the barks of *Cinnamomum camphora* in Residential Districts. Although some urban green space has a good environment and a vast green area, the heavy metal content in the barks of *Cinnamomum camphora* was high because of the influence of living waste and the surrounding environment.

- Bark has broad application prospects in monitoring environmental heavy metal pollution, but the current research is far from enough. Combining various biological monitoring methods (e.g., moss, leaves, barks, and roots), improving testing techniques and seeking more geochemical means will be the direction of future efforts.

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