Biological Monitoring Significance of Manganese in Barks of Xiangtan City

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Abstract. The content of Mn in barks of Xiangtan City was determined by Flame Atomic Absorption Spectrometry. The results showed that: (1) Xiangtan City belongs to the heavily polluted area of manganese. The average content of manganese in the bark is about 170 mg/kg and much higher than that of the background value of China (59.94 ± 7.15 mg/kg). (2) The Mn content of the bark showed the status of Mn pollution in Xiangtan. Thus, The barks are proper for a biological monitoring carrier for heavy metal content in this area; (3) Different barks have different and stable accumulation capacity for heavy metals.

1. Introduction

With the acceleration of urbanization, people often emit heavy metals into the environment in various ways, such as transportation, industry, fossil fuels, agriculture, and so on [1-5]. Heavy metal elements have a wide range of sources and a large number, and their harmful forms to the human body are also complicated. With the improvement of technology, the research object of heavy metal pollution has gradually shifted from soil and water to organisms, especially plants. "Biological monitoring" refers to the use of feedback generated by biological communities, populations or individuals on environmental pollution or transformation to show the pollution status, and provide a basis for the monitoring and assessment of environmental quality from a biological perspective.

As an alternative method to study environmental heavy metal pollution, people use plants more and more widely for biological monitoring. Nowadays, people frequently utilize lower plants, such as moss, algae, lichen, and so on, as biological monitoring of heavy metal pollution in the urban environment [6-9]. Wu Yanfang used moss to monitor heavy metal pollution in the atmosphere [10]. Except for lower plants, higher plants can also be used to detect the accumulation and distribution of heavy metals. Gaudry et al. studied the accumulation of zinc and manganese in the barks of Cedar of Lebanon [11]; Rusu et al. investigated the accumulation of zinc and manganese in hornbeam bark [12]; Kuang et al. studied the concentration of zinc and manganese in the bark of Pinus massoniana (Lamb.) [13]. Although plants can enrich and absorb heavy metal, there are distinct differences due to different organs and different kinds of heavy metals. Generally speaking, bark and root have the best ability to accumulate and absorb heavy metals in all organs of tree species. For the bark of a tree, it is usually exposed directly to the environment for a long time, and its residence time is even longer than that of leaves. So, it may be more representative [14]. From the existing literature, many studies focus on the determination of whether the bark of a tree is suitable for a carrier of biological monitoring by studying the heavy metal content in the bark of a tree species. Of course, there are also studies on the
full utilization of heavy metal content in the bark of different species to monitor pollution in a specific area.

China is a highly polluted area of Mn, with an average concentration of 59.94 ± 7.15 mg/kg [13]. Xiangtan is a primary industrial base in Hunan Province, which mainly develops metallurgy and chemical industry. It has a very famous heavy metal industry such as Xiangtan Manganese Mine in China. Therefore, Mn is a major heavy metal pollution element in Xiangtan City, which has attracted much attention for a long time [15, 16]. By measuring the content of heavy metals in the bark of different tree species (random), this article discussed the biological monitoring significance of heavy metals in the bark.

2. Study area
This study covers the urban area of Xiangtan City, Hunan Province, including Yuhu District and Yuetang District (Figure 1).

![Figure 1. Schematic diagram of the study area.](image)

The overall terrain of Xiangtan City is high in the west and low in the east, with many types of landform, such as mountains, hills, plains, and so on. The region belongs to the middle subtropical monsoon humid climate. It is prone to drought in the summer and autumn, while it is prone to cold waves and strong winds in the winter and spring. By 2014, 36 minerals have been found and identified in the city, and 16 minerals have been proved reserves, such as manganese, iron, quartz sand, potassium feldspar, barite, and other metal ores.

Yuhu District, located in the northwest of Xiangtan City, covers an area of about 451 km², including nine townships, eight streets, a National Economic and Technological Development Zone and an agricultural, an Agricultural Industry and Trade Group. Yuetang District lies in the northeastern end of Xiangtan City, where is the junction of the Xiangjiang River and the Lianshui River. It includes an area of 206 km² and covers 13 streets, one town, and three townships.

3. Sampling and Testing
3.1. Sampling
Xiangtan has many kinds of trees, and the most common ones are *Camphor, Magnolia grandiflora* L., Cherry blossoms, Pine, French Platanus, *Osmanthus fragrans*, Ginkgo, and so on. However, the distribution of these tree species is very uneven, and the planting years are different. Bark collection is difficult. Therefore, in the process of sample collection, according to the specific environmental conditions, trees were randomly selected, and the final samples mainly included the bark of *Camphor, Pine*, and *French Platanus* (Figure 2).

![Figure 2. Representative tree species.](image)

Thirty samples were collected from 12 sites, including Hunan Urban Construction College, Tianfu Cemetery, Xiangtan University, Yuhu Park, Yangmeizhou Water Park, Yuetang Park, Long-distance Bus Station, Longpai Food Limited by Share Co.LTD, Xiangtan Iron&Steel Co.LTD of Hunan Valin, Huxiang Park, Changcheng Color Printing and Public Security Bureau. When sampling, the bark with a diameter of not less than 20 cm and a distance of more than 1 meter from the ground was selected. Firstly, remove the adherents on the bark surface with a hard brush, and then get rid of bark with a stainless steel blade. The collected bark was packed into a sample bag and sent back to the laboratory for testing.

3.2. Sample Processing
Firstly, grind the contact surface between the blade and bark with sandpaper to reduce the impact of heavy metals on cutting bark with stainless steel blades, then dried continuously for 12 hours under 130°C until the sample was thoroughly dried to a constant weight. The dried samples were ground in an agate mortar and passed through a 100 mesh nylon sieve. Ground samples are stored in polyethylene self-sealing bags for testing.

The 0.5 g specimen was weighed and packed in the digestion bottle (three parallel samples). Then, 5 ml hydrochloric acid, 2 ml nitric acid and 1 ml hydrogen peroxide were added into each digestion bottle. The samples were digested by a microwave digestion instrument. The digested samples were placed in a PTFE crucible and heated on a heating plate at 300°C for more than 2 hours. During this period, distilled water is continuously added to avoid the sample in a dry heating state, and then filtered and fixed volume to 100 ml for testing.

3.3. Tests
The content of heavy metals in samples was determined by a Flame Atomic Absorption Spectrometry. When testing, there is one blank sample in every five groups, and the error between parallel samples is less than 5%.
4. Results and analysis

Even now, the research on the content of heavy metal in the bark is not mature in many aspects and lacks a unified background value. Due to far from the city center, and belong to a cultural and educational area, this paper takes the content of Mn in the bark of Xiangtan University as the background reference value for comparative study.

4.1. Content of Mn in Different Sampling Site

The average concentration of Mn in the study area was 37.42 mg/kg to 373.22 mg/kg. The minimum value was 37.42 mg/kg (Hunan Urban Construction College), and the maximum amount was 373.22 mg/kg (Public Security Bureau) (Figure 3). On the whole, although the content of Mn varies significantly in all 12 locations, there are some connections.

![Figure 3. Mn content.](image)

The content of Mn in the five sampling sites (Public Security Bureau, Changcheng Color Printing, Xiangtan Iron&Steel Co.LTD of Hunan Valin, Longpai Food Limited by Share Co.LTD and Long-distance Bus Station) was more than 200 mg/kg, which was twice higher than that at Xiangtan University, indicating that Mn pollution was severe. Among them, the content of Mn in the Public Security Bureau (Yuetang District) is exceptionally high, about three times higher than that in Xiangtan University, which is severe contamination. Field surveys found although most of the nearby residential areas were newly built, with fewer pollution sources and shorter construction time of nearby highways, the trunks of trees (roadside trees) were thicker, which indicate its bark exposure may take a relatively long time. Therefore, the following factors may be the reason of the severely over-standard manganese content in this area: (a) the long age of trees, the long time of bark and air contact in this area and (b) most of the pollutants may come from the pre-construction or comprehensive construction process of this area.

Except for Yuetang Park, other parks (Yangmeizhou Water Park, Huxiang Park, Yuhu Park) have Mn content ranging from 200 mg/kg to 100 mg/kg. However, the content of Mn in Yuetang Park is about 200 mg/kg, twice as much as that at Xiangtan University, which is obviously higher than that in other parks and pollutes heavily. The reason is that although it is a park with more vegetation and better environmental quality, on the one hand, it lies in the old industrial zone of Xiangtan City, on the
other hand, its east, west, north, and south are iron and steel industry, switch factory, electrical machinery plant and pharmaceutical company, respectively.

4.2. Mn Content in Different Functional Regions
This research divided the study area into four regions, namely Industrial Area (Longpai Food Limited by Share Co.LTD, Changcheng Color Printing, Xiangtan Iron&Steel Co.LTD of Hunan Valin), Traffic Intensive Area (Long-distance Bus Station, Public Security Bureau), Park Area (Yuetang Park, Yuhu Park, Yangmeizhou Water Park, Huxiang Park) and Suburb Area (Hunan Urban Construction College, Tianfu Cemetery). Figure 4 shows the average content of manganese in each functional area.

![Figure 4. The Content of Mn in Different Functional Regions.](image)

The content of Mn in each functional area of Xiangtan City is Industrial Area > Traffic Intensive Area > Park Area and Suburb Area. In regions with few human activities, the accumulation of Mn is less. Therefore, preliminary analysis shows that the primary source of Mn accumulation may result from human activities. The average content of Mn in the Industrial Area is 248.72 mg/kg and much higher than that in Xiangtan University (82.65 mg/kg), which indicates critical manganese pollution. Mn may mainly come from pigments (Changcheng Color Printing), iron and steel production (Xiangtan Iron&Steel Co.LTD of Hunan Valin) and industrial waste. The average content of Mn in the Traffic Intensive Area is 211.98 mg/kg, which indicates an Mn pollution, but the pollution degree is lighter than that in the Industrial Area. Human activities are frequent in this region, and the combustion of fossil fuel (e.g., Long-distance Bus Stations) is likely the primary origin of Mn. The average content of Mn in the Park Area is 172.36 mg/kg, which has been slightly polluted by Mn. Although there is more vegetation in the Park Area, the source of Mn is complicated because it is close to the urban area. The content of Mn in the Suburb Area is only 42.48 mg/kg, which is less than that in reference point (Xiangtan University). Apparently, far away from the two primary manganese sources (Traffic Intensive Area and Industrial Area) may be the main reason for the low manganese content in this area. Although there are still Mn from pesticides and fertilizers, the amount is much smaller, which indicates no Mn pollution. Generally speaking, the dust produced in the mining process of manganese mine aggravates the contamination of Mn in Xiangtan City.

4.3. Biomonitoring Significance of Bark on Heavy Metals
Kuang et al. thought that the average concentration of manganese was 59.94 ± 7.15 mg/kg [13], while the average amount of manganese in Xiangtan was about 170 mg/kg, which was far beyond the average level. Hence, Xiangtan City is a region with severe manganese pollution. Bowen pointed out that the acceptable limit of manganese content for plants ranged from 20 mg/kg to 700 mg/kg [17]. Although Xiangtan is a heavily polluted area of Mn, its Mn content is still within an acceptable range. Xiangtan bark is suitable for biological monitoring of heavy metals in this area.

However, the content of Mn in the bark of different tree species in the same place is also different. Taking Camphor and French Platanus in Public Security Bureau, Xiangtan Iron&Steel Co.LTD of
Hunan Valin and Longpai Food Limited by Share Co.LTD as examples, this paper attempts to explore the similarities and differences of heavy metal accumulation in different tree species.

**Figure 5.** Comparison of Mn Content in Bark between *Camphor* and *French Platanus*.

Although the bark of *Camphor* and *French Platanus* in different locations contains a certain amount of Mn, the content of Mn in the bark of *French Platanus* is less than that of *Camphor*, and the difference of Mn content between them is almost the same (Figure 5). In other words, the accumulation of Mn in the bark of *French Platanus* is not as good as that of *Camphor*, and the adsorption capacity of these two barks to heavy metals does not change with places (relatively stable). The main reason may be related to their bark structure. The bark of *Camphor* is green and smooth when it is young. With the growth and coarsening of branches, its color gradually changes to yellowish brown or greyish brown, and there are many deep groove cracks, and the bark is loose. This structure facilitates the adsorption and accumulation of heavy metals (Figure 6). When the *French Platanus* is young, its bark wraps the trunk tightly. When the tree trunk becomes thicker, the bark gradually becomes thin, aging and falling off, which is a phenomenon of life of *French Platanus* (Figure 6). The bark shedding is not only due to the growing needs of the *French Platanus* but also related to the weather. For example, after several days of continuous rain and sudden exposure to the sun, the bark of *French Platanus* tends to dry and curl and accelerate peeling [18]. This characteristic is not conducive to the long-term accumulation of heavy metals, because the primitive accumulation of heavy metals will lose with the bark shedding. Therefore, the collection of heavy metals in the bark of *French Platanus* is worse than that of *Camphor*. Of course, which bark has the best adsorption capacity and which bark is the most suitable carrier for heavy metal biological monitoring needs further study.

**Figure 6.** The trunk and bark of *Camphor* and *French Platanus*.

5. Conclusion
The study of manganese content in the bark of Xiangtan City reveals that:
(1) Xiangtan belongs to Mn contaminated area. The average content of manganese in the bark is about 170 mg/kg, which is much higher than the average concentration of manganese (59.94 ± 7.15 mg/kg). The government, industrial producers and citizens should attach great importance to it and try their best to control it from the source to reduce the pollution of manganese.

(2) The bark in Xiangtan is suitable for acting as a biological monitoring carrier for heavy metal in this area. The content of Mn in bark showed the status of Mn pollution in Xiangtan, and it can be used to assess the environmental quality of this area and carry out pollution warning.

(3) Different bark had different accumulation ability of heavy metals. Comparing the Mn content in the bark of Camphor and French Platanus in three different locations (Public Security Bureau, Xianggang, and Longpai Sauce Industry Group), the Mn content in the bark of the same tree species was distinct in different sites. For the same place, the Mn content in the bark of different tree species was different. Besides, the difference value between the Mn content in the bark of the two tree species was relatively stable.

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