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# Tree ring analysis for determination of pollution history of Chengde City, north China

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**Abstract**—Air pollution history of sulphur and heavy metals since 1800 in Chengde City, north China, was studied by analyzing the concentrations of sulphur and heavy metals in growth rings of *Pinus tabulaeformis* Carr. Sulphur concentrations in the tree rings of 1910—1920, 1970—1980, and 1980—1990 have increased 1—2, 3—5 and 10 times respectively as those in the tree ring of 1810—1820 ($P<0.05$). This is ascribed to the result of urbanization, especially the appearance and aggravation of industrialization, in the city of Chengde since 1950s. Fe appeared to increase during 1920—1940, possibly due to the opening of Damiao Iron Mine by the Japanese in 1927; Mn increased throughout the whole history, from 4.1 μg/g (1840—1850) to 10.4 μg/g (1980—1990, $P<0.05$); Pb did not increase until 1980 but increased sharply during the last 10 years by 560% ($P<0.001$). This is caused by the increased number of automobiles in the city. The contents of Cu, Zn, Ni have changed little. The concentrations of sulphur and heavy metals in the tree rings at the beginning of 1800s were the lowest and could be regarded as the background concentrations. We calculated that S, Fe, Pb, Mn, Ni, and Zn in the tree rings have increased 10, 2.4, 1.8, 1.5, 1.0 and 0.8 times respectively during the past 190 years or so. The results showed that serious environmental pollution, especially air pollution of $SO_2$, has occurred since 1949 when the People's Republic of China was founded.

**Keywords**: tree rings; *Pinus tabulaeformis*; sulphur and heavy metals; pollution history; Chengde City.

## 1 Introduction

For the past few decades, scientists have carried out extensive research in the Arctic and Antarctic areas, where ice and frozen soils, as well as lake sediments with a long history, are sampled to reveal large-scale environmental changes. Some even have paid attention to the literal records of burning coals, mining processes, or pollutant displacements to find the pollution history. These methods, however, have their limitations due to their uncertainties in the determination of the exact pollution history of a particular area. Lepp (Lepp, 1975) reported that the growth rings of tree could be the best way to solve such difficulties. His hypothesis was that air pollution caused injury and growth-decline even death of tree, which could be reflected in the tree rings, such as elevated pollutant concentrations. Before that time, tree ring analyses were used in studying climate changes (Cook, 1975). Tree barks were successfully used to indicate lead pollution process caused by mining activities (Sheppard, 1975). However, for a longer history of environmental changes, xylem tissue is more useful, because the effects of air pollution at a particular time can be known by analyzing the tree's growth or pollutant concentrations in the xylem formed during the same time intervals (Ward, 1974; Lepp, 1975; Baes, 1981; Albasel, 1985).

In China, tree rings were formerly studied for their functions in indicating climate changes (Liu, 1982; Wu, 1988; Xia, 1991). In this paper, we try to use their functions in revealing pollution history of a city. The study site is located in Chengde City (4°68'N, 117° 56'E), where the largest existing imperial garden, the Summer Villa estate, is located. The city has a history of less than 300 years and a population of 300000 now. The pine trees *Pinus tabulaeformis* Carr., planted of Qianlong and Jiaqing Years (1760— 1815, Jiang, 1990) are nearly of the same age of the city. So, the concentrations of pollutants in the tree rings may give us useful information for the revelation of the air pollution history of Chengde City.

# 2 Materials and methods

## 2.1 Sampling

The study was carried out in the Summer Villa estate, Chengde City. Dead tree (with no green needles) of *Pinus tabulaeformis* Carr. (died in 1990) from four sites of the estate were sampled (Fig. 1). Bifengmen, Guli Gebei and Songyunxia are located in the Hill Area, and Jinshanting in the Lake Area (Jiang, 1992). The soils of each site are clayey soil (Bifengmen), brown earth (Guli Gebei and Songyunxia) and fluvio-aquic soil (Jinshanting), and their pH values were 8.20, 8.10, 8.04 and 7.40, respectively (Jiang, 1990b). The rea-

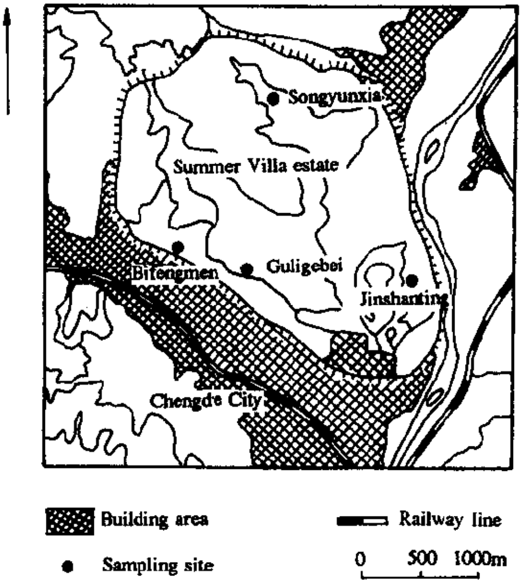

Fig. 1 Location of the Summer Villa estate in the city of Chengde, showing the tree ring sampling sites. Bifengmen, Guli Gebei and Songyunxia are located in Hill Area, with the soils being clayey soil and brown earth, respectively; Jinshanting is located in the Lake Area, with fluvio-aquic soil

sons for the death of pine trees of the study area can be attributed to mechanical destruction, worsening of the habitat, insect grazing, and most importantly, the serious air pollution (especially $SO_2$) in the city (Jiang, 1990). Four dead trees from the four sites were cut down, and discs with a thickness of 30 cm were cut at breast-high trunk level.

By counting the tree rings (the rings were distinct enough for counting), we estimate that their ages are 189, 175, 187 and 230 years old respectively for Bifengmen, Guli Gebei , Songyunxia and Jinshanting. The ages of the four dead trees are much younger than their natural life-span, probably 600 years or more, since a 600- year-old tree of that species was reported still alive in Beijing, some 200 km south-west of Chengde (Jiang, 1990).

The discs were firstly marked with tiny nails driven in every 10-year thickness, and then peeled off. For every 10-year section, five 5g samples of xylem were obtained. Total 180 samples were obtained from the four dead trees. All the samples were oven-dried to constant weight at 80℃ then ground.

### 2.2 Chemical analysis

1.5g samples were weighted and ashed at 450℃ for 8h. After cooling, and 5 ml $HNO_3$ and digest on a electrical plate stove, for about 4 hours. Then the digestion solutions were washed with 0.2 mol/L $NO_3$ into 25 ml tube, and stored in plastic bottles of the same volume. For chemical analysis, total S was measured by $BaSO_4$ Turbidity Method; Pb and Ni were performed on a Perkin Elmer 703 Atomic Absorption Spectrophotometer, and Fe, Zn, Cu, Mn by Y2-Flame Absorption Spectrophotometer (Jiang, 1990b).

### 2.3 Quality control and quality assurance

As long as the samples were chemical analyzed, the standard plant materials (woody plant) produced by the Institute of Geophysichemical Survey, China National Department of Mining, were simultaneously digested and chemically analyzed. Six groups of standard materials (three replications in each group) were analyzed, yielding the mean concentrations within the permissible ranges of standard values (Table 1), and hence indicating that the analytical methods we employed were reliable.

**Table 1 Comparison of chemical analysis of the standard plant materials with the standard values**

**(S, mg/g; heavy metals, μg/g)**

| Elements | Standard values | First group | Second group | Third group | 4th group | 5th group | 6th group | Average |
|---|---|---|---|---|---|---|---|---|
| S | 3.2±0.2 | 3.67 | 3.13 | 3.31 | 2.56 | 3.13 | 3.16 | 3.16 |
| Cu | 5.2±0.3 | 5.49 | 5.54 | 5.52 | 5.52 | 5.51 | 5.36 | 5.53 |
| Fe | 1020±40 | 969.87 | 985.48 | 971.59 | 975.15 | 981.08 | 976.16 | 976.56 |
| Zn | 20.6±1.0 | 19.74 | 19.92 | 21.40 | 21.44 | 21.61 | 21.63 | 20.96 |
| Mn | 52±3 | 48.74 | 49.08 | 53.14 | 51.64 | 53.14 | 52.05 | 51.22 |
| Ni | 1.4±0.3 | 1.41 | 1.23 | 1.59 | 1.51 | 1.59 | 1.29 | 1.33 |
| Pb | 8.1±0.7 | 8.12 | 8.53 | 7.90 | 8.05 | 7.90 | 7.76 | 8.06 |

### 2.4 Statistical analysis

Statistical analysis for the comparison of element concentrations among different times was carried out by using the software system for data analysis (SAS) procedures. Analysis of variance (ANOVA) procedure was used for the multi, pairwise comparisons. The 0.95, 0.99 and 0.999 confidence limits of differences between the means were employed.

## 3 Results and discussion

### 3.1 Changes of sulphur concentrations in the tree rings

Among the four sampling sites, it was shown that the lowest concentration of S, 41.8 μg/g, was from tree rings of *Pinus tabulaeformis* Carr. at Jinshanting site formed during 1771—1780, while the highest S concentration, 572.9μg/g, was from the tree rings formed during 1986—1990 from Bifengmen site, 14 times higher than the former. All the samples showed the lowest concentrations occurred at the end of eighteenth and beginning of nineteenth century (1760—1820) and began to increase at the beginning of this century (1910—1930). The S concentrations in the tree rings formed during 1910—1920, 1970—1980, and 1980—1990 have increased 1—2, 3—5, and 10 times, respectively, as those in the tree rings of the 1810— 1820 ($P<0.05$, Fig. 2). Compared with the background (formed in 1800—1820), the S concentration in the tree rings during the last 10 years is elevated by 12, 9, 8 and 6 times, respectively, in Bifengmen, Songyunxia, Jinshanting and Guli Gebei ($P<0.05$). Bifengmen showed serious atmospheric $SO_2$ pollution in history, as indicated by the large increase of S in the xylem. This could be due to the fact that this site was the gate of the estate, and was only 50m from the city's residential area that contributed much of the $SO_2$ emissions owing to coal-burring (Jiang, 1990a). During 1934—1943, tree rings in the Bifengmen site showed largest S concentration, 370.1 μg/g, while the S concentration of tree rings formed in the same period of time from the other three sites ranged only from 66 μg/g to 106.6 μg/g. We attribute this to the wars and fires caused by the invasion of Chengde City by the Japanese (1927— 1945). Trees at this site were seriously burned with marks still distinct even today (Jiang, 1990).

For all the sites, xylem S concentrations appeared to have gradually increased with time (Fig. 2), being consistent with the expansion of urban areas and population growth (Fig. 3). Chengde has a history of less than 300 years. In 1674, it was not shown on the map of Qing. In 1703, the Summer Villa estate was built. The city was developed from a little village with a couple of families. But as soon as the estate was established, the population began to increase rapidly. The majority of the people in the Chengde City now are descendants of estate-building workers and immigrants from neighboring Shandong and Henan provinces, who immigrated when natural famine occurred.

The increase of the city's population could be divided into following stages: from 1703 to 1707, several hundred people moved in; 1707—1778, the city's population almost tripled, although the total number in the city was less than 10000. The most dramatic increase of population occurred during the last 50 years. For example, from 1949, when the People's

Republic of China was founded, to 1957, the population increased from 60000 to 120000 (not including farmers); it was 240000 in 1971, and more than 330000 in 1988 (Fig. 3).

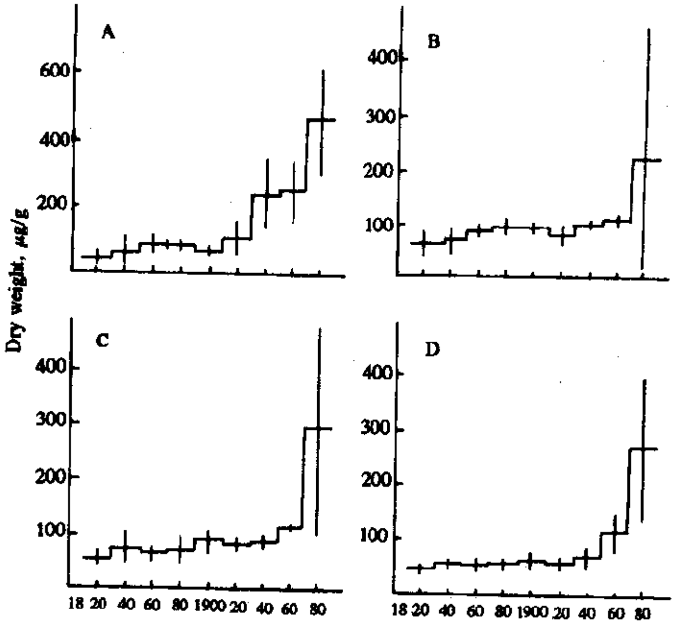

Fig. 2 Sulphur concentration in the xylem of tree rings of *Pinus tabulaeformis* Carr. formed in different historical periods at four sites of the Summer Villa estate, Chengde City, north China, bars representing the standard error
A: Bifengmen B: Guli Gebei C: Songyunxia D: Jinshanting

Therefore urbanization in Chengde City occurred with the establishment of the imperial garden, Summer Villa estate (1703), but increased rapidly during 1950s. After that industrialization began to develop. Before 1949, there was few industries except for a pot-making factory and few handicraft mills plus the Damiao Iron Mine opened by the Japanese (1927—1945), 20 km from the city. From 1949—1989, the city's decision-makers thought highly of the development of industry, and 330 factories have been set up within the 17. 6 km$^2$ city area. This has caused severe air pollution due to SO$_2$ emissions and the production of other suspended particles.

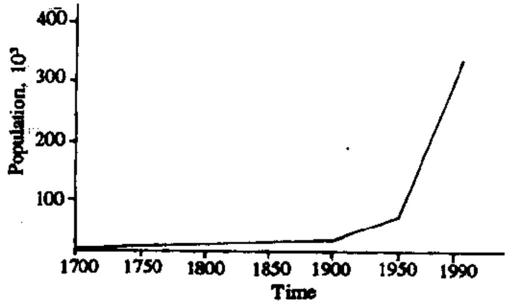

Fig. 3 Change in population of Chengde City since 1700

Increase of SO$_2$ in the air can cause increased levels of sulphur is tree rings. This is because the S in the SO$_2$ may deposition the soil and tree roots take up the S. The S will then move, via the transpiration stream, into the xylem. The trace metals may be taken this way, too. Some of the mechanisms, however, is quite unclear, for example, we still do not know if the woods get the S from the stomata of needles. Besides, the absorbed air SO$_2$ as well as the metabolically derived substances (inorganic sulphate, amino acids, proteins, sulpholipids) may not irreversibly fix with a certain section as is in the rings. Moreover, excess sulphur in the plant may be converted to gaseous $H_2S$ and released into atmosphere or may be released, as sulphate, into the soil via the roots (Rennenberg, 1984). Even so, in this study, the rapid increase of S in rings with the process of urbanization can indicate that serious sulphur pollution has occurred in Chengde City.

### 3.2 Changes of heavy metals in the tree rings

#### 3.2.1 Cu

Cu has increased in the xylem of *Pinus tabulaeformis* Carr. formed after 1870 (Fig. 4) from 7.1 μg/g (1820) to 19.6 μg/g (1940; $P<0.05$). Before that time, Cu had not seemed to be as low as we expected. It did not increase in the last 20—30 years; rather it decreased to 5 μg/g, lower than that of 1820. Such a result indicated that Cu in Chengde City was not the main environmental pollutant.

#### 3.2.2 Fe

It can be seen from Fig. 4 that Fe concentrations during 1810— 1820, 1990—1920, and 1950—1960 were all less than 70 μg/g, and there has been no increase in the history of Chengde City ($P>0.05$), except in the periods 1850—1870 and 1920—1940. We believe that the increase in 1850—1870 was due to the fast growth of pine trees which led to fast absorption for minerals. In 1920—1940 the increase can be related to the opening of the Iron Mine Factory by the Japanese (1927—1945). In that stage the tree rings had the highest Fe concentration, 128 μg/g; after that it began to decrease. Even so, the much larger Fe concentration in 1980—1990, 103 μg/g indicated impacts of industrialization of the city during last few decades.

#### 3.2.3 Zn

The tree rings had the lowest Zn concentration, 8.4 μg/g, during 1810—1820, and the highest, 18.7 μg/g in 1930—1940. After 1810, Zn appeared to increase and began to decrease after 1950. But a mild increase after 1980 could also be found (Fig. 4). During 1840—1940, Zn had a relatively higher concentration, averaging 13.7 μg/g, 60% more than that of 1810— 1820. We conclude that Zn is not the main pollutant of Chengde, because the Zn concentrations in the tree rings have kept relatively constant during the last 100 more years, and they fall within the normal range of Zn concentrations in the plant tissue. For crops and above ground tissues of grasses, when Zn exceeds the level of 27—120 μg/g, it will lead to plant injury (Baes, 1984). It is still unknown if Zn causes damage to woody plants. In our case study of tree rings of *Pinus taulaeformis* Carr., average concentration of Zn appeared to be 10—20 μg/g and the highest concentration was 28.1 μg/g, which occurred during the vigorous growth of the pine trees and was found harmless to the growth.

#### 3.2.4 Mn

From the beginning of 1820, Mn began to increase from 4.1 μg/g (1820—1830)to 10.4 μg/g (1980—1990), an increase by 2.5 times ($P<0.05$, Fig. 4). And the highest content was found with the last 10 years.

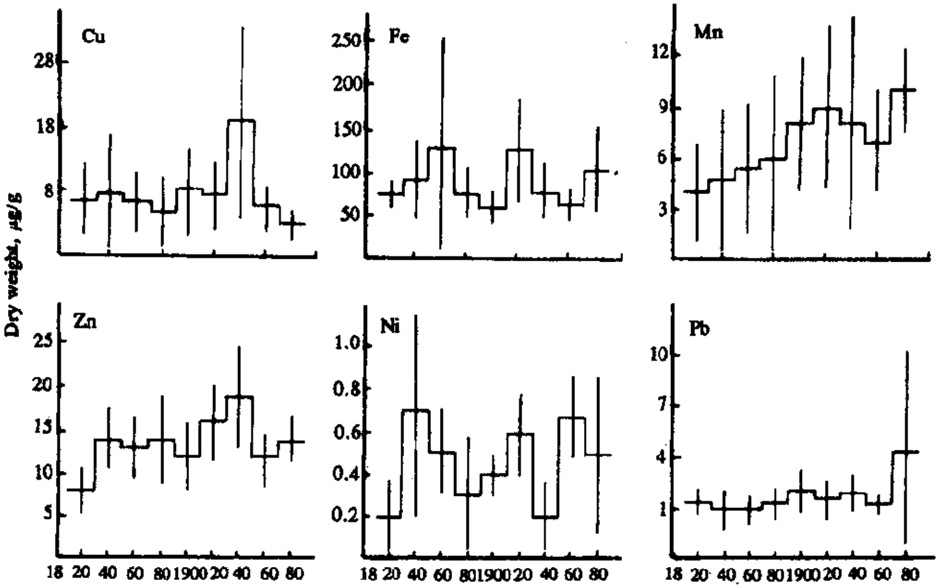

Fig. 4 Concentrations of Cu, Fe, Zn, Mn, Ni, Pb in the xylem of tree rings formed in the different historical periods at the Summer Villa estate, bars representing the standard error

The normal range of Mn concentration in the plant tissue is 10— 100 μg/g (for example, 20—30 μg/g for rice) and 0. 01—0. 05 μg/$m^3$ in the urban atmosphere. When concentrations in crops and the aboveground tissues of grasses exceed 150—450 μg/g, plant damage will occur (Baes, 1984). Although the concentration of 4—10 μg/g in the tree rings may not cause injury to the growth of pine tree, the consistency of the increase of Mn with the expansion of urbanization and industrialization indicates such an increase is an good indicator of environmental change.

### 3. 2. 5 Ni

Like Fe, Ni did not show an increasing trend throughout the history of Chengde City (Fig. 4). The lowest, 0. 18 μg/g, was found in 1810—1820, while the highest 0. 67 μg/g, was found in 1840—1850, 1940—1950. The difference between maximum and minimum was 340%, with a range of 0. 20—0. 50 μg/g, though they were not statistically significant ($P>$ 0. 05).

Excessive amounts of Ni inhibit absorption of Fe by plants, resulting in chlorosis and curled leaves or even death of the plants. The natural concentration of Ni in the earth's crust is 75 ppm, while the concentration of Ni in the soils is <10 ppm. The Ni concentration in the plant is within ppb level (Jin, 1991). From the results of our study, Ni seems to be stable, indicating that Ni concentration in the tree rings may not be a sensitive indicator of air pollution. Alternatively, the city has no serious environmental Ni pollution.

### 3. 2. 6 Pb

In an urban area, Pb comes mainly from gases of car exhaust. Since 1930, tetraethyl lead has been popularly used as anti- explosive additive, so the increase of air Pb shall be obvious after 1930. In the United States, it was found that Pb significantly increased in the tree rings formed after 1930 (Ward, 1974; Kardell, 1978). But in Chengde there was no such an increase between 1920 and 1940 (Fig. 4). Only during 1940—1950, Pb appeared to increase, from 1.64 μg/g (1920—1930) to 1.92 μg/g ($P>0.05$), and the concentration was even lower than that of 1900s, which was 2.15 μg/g. The largest Pb concentration, 4.27 μg/g, was found in xylem formed during the last 10 years, which was 5.6 times more than that of 1920—1930 ($P<0.001$).

The natural Pb concentration in the earth's crust is 16 ppm; 2— 200 ppm is in the soils (but could be 300 ppm for urban soils), and <0.5 μg/m$^3$ is in the atmosphere (but could be 40 μg/m$^3$ in urban areas with heavy traffic; Jin, 1991). The significant increase of Pb during the past 10 years is the best indicator for Pb pollution of the Chengde City.

### 3.3 The background concentrations of sulphur and heavy metals in *Pinus Tabulaeformis* Carr.

Fig. 2 and Fig. 4 show that concentrations of S and heavy metals in the tree rings of *Pinus taulaeformis* Carr. formed at the beginning of nineteenth century (1810—1820) were the lowest. Such concentrations can be regarded as the natural background of *Pinus taulaeformis* Carr., i.e., S, 45—50 μg/g; Cu, 2—8 μg/g; Fe, 30—60 μg/g; Zn, 7—11 μg/g; Mn, 3—7 μg/g; Ni, 0.1—0.4 μg/g and Pb, 0.4—2.0 μg/g. Compared with background concentrations, S in the xylem now (1980—1990) has increased 10 times. The concentrations of Fe, Pb, Mn, Ni, and Zn (averaged from the four sites of Table 2) have increased 2.4, 1.8, 1.5, 1.0, 0.8 times, respectively (Table 2).

**Table 2 Comparison of concentration of S and heavy metals in the tree rings of *Pinus taulaeformis* Carr. formed during 1810—1820 and 1980—1990, and sampled from the Summer Villa estate**

| Sites | Years | S | Cu | Fe | Zn | Mn | Ni | Pb |
|---|---|---|---|---|---|---|---|---|
| Songyunxia | 1816—1825 | 51.9 | 4.8 | 49.1 | 11.8 | 4.8 | 0.09 | 0.42 |
| | 1986—1990 | 451.1[c] | 4.9 | 161.9[b] | 16.7[c] | 6.0 | 0.36 | 0.39 |
| Bifengmen | 1803—1813 | 46.9 | 4.8 | 63.5 | 11.8 | 4.8 | 0.33 | 1.56 |
| | 1984—1990 | 572.9[c] | 4.8 | 140.5[c] | 11.8 | 11.6[b] | 0.47 | 14.45[c] |
| Guli Gebei | 1812—1821 | 46.8 | 7.5 | 56.4 | 6.9 | 3.7 | 0.14 | 2.31 |
| | 1982—1990 | 285.5[c] | 2.1 | 49.4 | 11.8[b] | 13.4[c] | 0.14 | 1.41 |
| Jinshanting | 1801—1810 | 46.9 | 4.8 | 35.3 | 10.1 | 7.6 | 0.06 | 0.81 |
| | 1981—1990 | 370.3[c] | 2.1 | 63.1[a] | 15.0[c] | 10.5[a] | 0.99[c] | 1.85[c] |

[a] $P<0.05$; [b], $P<0.01$ [c], $P<0.001$

## 4 Conclusions

Tree ring analysis can be used to indicate past pollution of a region. In this study, we have measured concentrations of sulphur and heavy metals (Cu, Fe, Zn, Mn, Ni, Pb) in the rings of four dead trees of *Pinus taulaeformis* Carr., sampled from the Summer Villa estate, north China. The study shows that sulphur concentrations in the rings of 1910—1920, 1970—1980, and 1989—1990 have increased 1— 2, 3—5 and 10 times respectively of those in the background concentration of 1810—1920 (51.9 μg/g, $P<0.05$). Fe appeared to increase during 1920—1940, an increase from less than 70 μg/g to 128 μg/g, which was due to the opening of an iron mine; Mn began to increase since 1820, from 4.1 μg/g (1820—1830) to 10.4 μg/g (1980— 1990, $P<0.05$); Pb is sharply elevated during the last 10 years, from 1.64 μg/g (1920—1930) to 1.92 μg/g (1980—1990, $P<0.001$), while concentrations of Cu, Zn, Ni have changed little. Compared with the background concentrations, S, Fe, Pb, Mn, Ni, Zn, in the tree rings have increased 10.0, 2.4, 1.89, 1.5, 1.0 and 0.8 times respectively during the past 190 years or more. The increase of the pollutants in the rings indicates that environmental pollution has occurred, and the pollution process is consistent with that of urbanization, especially during the last 10—20 years.

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