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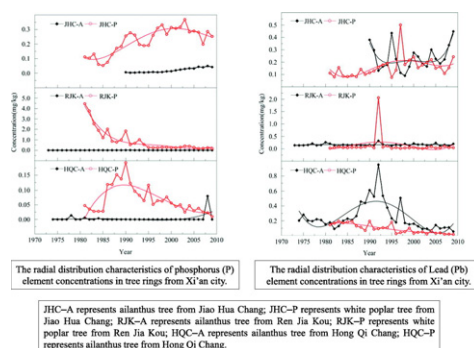
## Elements content in tree rings from Xi'an, China and environmental variations in the past 30 years

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### HIGHLIGHTS

- Using ICP-MS and ICP-AES, the concentrations of chemical elements in tree rings from Xi'an, China, were analyzed.
- Variation trends of concentration of Pb and Cd in tree rings were consistent with that of their growing environment.
- P and Zn were translocated within tree rings to a certain degree.
- White poplar with a stronger absorptive capacity for Cd and Zn is a suitable species in environmental remediation.

### GRAPHICAL ABSTRACT



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### ABSTRACT

Using inductively coupled plasma mass spectrometry (ICP-MS) and inductively coupled plasma atomic emission spectroscopy (ICP-AES), the characteristics of chemical elements were analyzed in white poplar (*Populus bonatii* Levl.) and ailanthus (*Ailanthus altissima* (Mill.) Swingle) from three sites in the town of Xi'an, China. The results indicated that the concentration variations of Pb and Cd in tree rings were consistent with that of the environment where the trees were growing. P and Zn were translocated within tree rings to a certain degree, which led to an inaccurate pollution reconstruction. We also found that white poplar had a stronger absorptive capacity of Cd and Zn than ailanthus, which could make white poplar better as a species in environmental remediation. From this research we can see the great potential of tree rings for studying the history of different element pollution in the environment, showing that dendrochemical methods could be used as a powerful component in environmental monitoring programmes, to reconstruct past pollution history at the time when monitoring systems were not yet installed.

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### 1. Introduction

The type and amount of chemical pollution in the environment has continuously increased due to the rapid development of the global

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economy, and its impact on ecosystems is becoming more and more alarming. To effectively control contamination, knowledge on the variations of polluting elements in the environment is urgently needed (Yang et al., 2012), making the current monitoring of urban environmental quality increasingly important. Because of the limitations and non-repeatability of the routine monitoring processes for the atmosphere, surface water, groundwater, and soil, it is difficult to record the contamination history in a city.

Dendrochemistry, the study of the chemical composition of tree rings, is a research field that can be used to investigate the contamination history and transportation of chemical elements in the environment. Since Lepp (1974) first put forward the concept of dendrochemistry and successfully reconstructed temporal trends of trace elements in the environment using tree rings, there has been great progress in using tree-ring records to reconstruct pollution history. An underlying assumption of dendrochemistry is that the chemical composition of an annual ring at least partially reflects the chemical composition of its environment at the time of its formation (Watmough, 1999). Many studies have verified the feasibility of tree rings as environmental monitors of chemical element transition and have demonstrated similar variation trends of elemental concentration in polluted environment and growth rings (Baes and Mclaughlin, 1984; Lagueard et al., 2008; Liu et al., 2009a; Mihaljevič et al., 2011; Xu et al., 2014; Lee et al., 2015). However, other studies have indicated that dendrochemistry could not reflect the chemical and elemental variations in the environment (Watmough and Hutchinson, 2003; Pearson et al., 2006). Even so, if we fully understand the basic principles of dendrochemistry and select suitable tree species using correct and appropriated sampling strategy, dendrochemistry is still a powerful tool for tracing polluting elements in the environment. Previous researches of dendrochemistry demonstrated that ailanthus (*Ailanthus altissima* (Mill.) Swingle) (Su et al., 2008) and white poplar (*Populus bonatii* Levl.) (Madejon et al., 2004; Berlizov et al., 2007) were good indicators for recording element variations in the environment.

In China, the history of air pollution was reconstructed for the last 200 years for the Beijing region based on records of pollution in tree rings (Nie et al., 2001). It was also found that element variations in tree rings were closely related to the history of industrial development in Shenyang (Anderson et al., 2000) and coal, iron and steel smelting, cement production and motor vehicle exhaust emissions are the main contributor of heavy metal pollution in Jinan (Gao et al., 2016). Using annual growth rings of native hardwood species, *Kalopanax septemlobus*, as the potential archive of the past Pb and Zn pollution events, Xu et al. (2014) reconstructed trace metal contamination history in the Yangtze River Delta region.

Ailanthus and white poplar are common tree species in urban areas in Xi'an City. We analyzed the concentration of five trace elements (Cd, Mn, P, Zn and Pb) in the tree rings of Chinese mahogany and phoenix from both the city and suburbs of Xi'an, as well as the contents of eight trace elements (Cr, Mn, Hg, Zn, Pb, Cd, As and P) in the tree rings of Chinese pines of eastern Xi'an (Liu et al., 2009a, 2009b). To comprehensively understand the environmental changes of chemical elements concentrations in Xi'an, we furthered this research. In this paper, the concentration of the elements of lead (Pb), cadmium (Cd), zinc (Zn), phosphorus (P), manganese (Mn), iron (Fe), copper (Cu), arsenic (As), tin (Sn), cobalt (Co), nickel (Ni), chromium (Cr), and mercury (Hg) were determined in tree rings of ailanthus and white poplar in Xi'an City in order to (1) investigate the variability of different chemical elements within and between trees, and thus better understand their biogeochemical behaviour in ecosystems; (2) assess if certain elements in tree rings are more reliable than others for monitoring environmental pollution; and (3) test the applicability of ailanthus and white poplar as environmental archives of element deposition. Outcomes of this study could serve as baseline data for future environmental impact assessment.

## 2. Materials and methods

### 2.1. The study area

Xi'an is located in the Guanzhong Plain on the edge of the Wei River at the foot of Qinling Mountains (107°40' – 109°49'E, 33°39' – 34°45'N). The study region is characterized as a warm and temperate semi-humid monsoon climate. Xi'an meteorological station (34° 18' N, 108° 56' E, elevation 397.5 m a.s.l., 1953–2004) shows that the annual precipitation is approximately 507.7 to 719.8 mm, with an average pH of 5.84. The mean annual temperature is 13.6 °C, and the prevailing wind is from the northeast. The soil in Xi'an City is alkaline (pH = 8.27) (Li and Feng, 2010). The soil in different areas within the city has been polluted mainly due to the development of industry and transportation (Han et al., 2008; Li and Feng, 2010).

### 2.2. Sampling sites and samples collection

To investigate the content of chemical elements in tree rings under different environmental conditions, three sampling sites were chosen to represent three contamination scenarios: industrial pollution, traffic pollution, and low-degree pollution (Fig. 1). The first sampling site, Jiao Hua Chang (JHC), was a chemical plant located in the western suburbs. The plant was put into operation in 1978 and stopped production in 2007. There were lots of industrial factories of different kinds around this site and several main roads nearby. The second sampling site, Ren Jia Kou (RJK), is approximately 70 m in distance from the West Second Ring Road and is characterized by heavy road traffic. Moreover, there was a small sewage ditch flowing past (the distance from the ailanthus was approximately 20 m, and the distance from white poplar is about 1 m). This site is mainly affected by automobile exhaust. The third sampling site, Hong Qi Chang (HQC), is near a purification plant at the northern suburbs, where little pollution is present, with coal gas and domestic garbage produced by residents being the main pollutant sources.

Trees are usually used as street greening and planting in cities, and felling trees is strictly prohibited by the local government. Therefore, the traditional dendrochronology sampling strategy (more than ten trees in an individual site) is not suitable for the dendrochemistry research in urban settings. In fact, there have been some practical examples that obtained ideal results with only a few representative tree samples (Prohaska et al., 1998; Kimberly and Anderson, 2002; Charlotte et al., 2006). In our study, sample trees had not been damaged by fire, drilling or other effects, growing healthily before being cut down (due to road construction).

Sampling was conducted in December 2009. Altogether, 3 ailanthus trees and 4 white poplar trees at JHC, 1 ailanthus tree and 1 white poplar tree at RJK, and 2 ailanthus trees and 1 white poplar tree at HQC were selected. Discs from ca. 30 cm above the ground in the main stem were taken. Meanwhile, 4 soil samples from each of the three tree sites were also collected at every 10 cm in totally 40 cm depth underground.

### 2.3. Experiment of prophase and acid digestion of plants

The growth rings of the discs were revealed by surface polishing using a belt sander. The discs were then dated and the ring widths from four directions were measured; the average ring widths were used to compute the correlation between elements. The discs were ultrasonically washed by Milli – Q water for 1 h in order to eliminate any adhered contaminants on the surface and then naturally dried. Every ring was then peeled with a thin stainless-steel blade. All instruments were rinsed with pure alcohol after the treatment of each sample.

All reagents were guaranteed to be reagent grade. All samples were cleaned with 10% HNO<sub>3</sub> before use. A 0.50 g sample was immersed in 8 mL of HNO<sub>3</sub> and 2 mL of H<sub>2</sub>O<sub>2</sub> in a 75 – mL PFA vessel for 12 h. Forty samples were digested simultaneously, including a standard

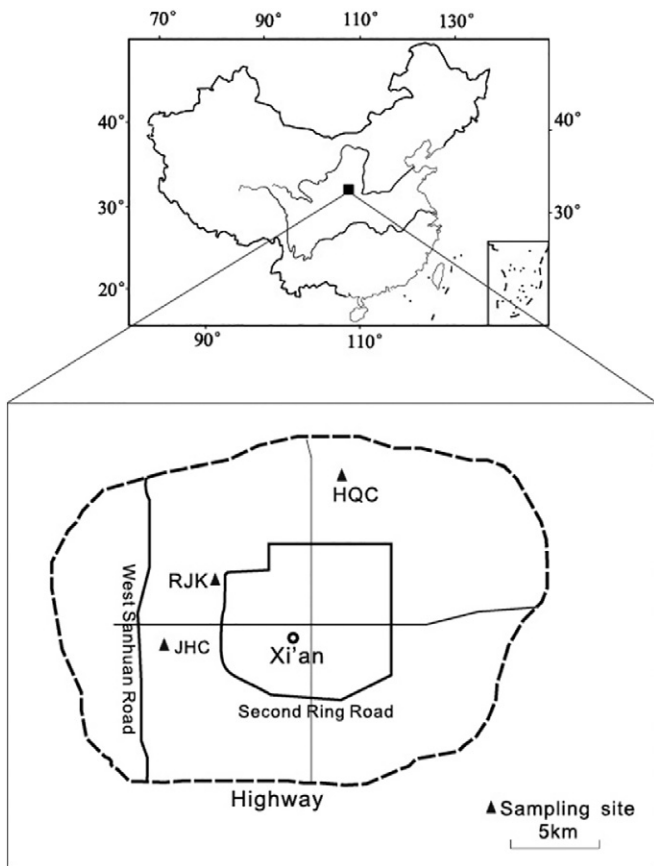


Fig. 1. Sampling sites.

material GSV – 2 (Shrub leaves; Institute of Nuclear Chemistry and Technology) and a blank sample. After cooling down, the mixture was transferred into the crucible and was then evaporated using an electric hot plate. When the volume of solutions reached 1 mL, 1 mL of concentrated  $\text{HClO}_4$  was added for further digestion (approximately 2 h). The solutions were then diluted with 5% nitric acid to a final volume of 25 mL and were subsequently filtered using 0.45  $\mu\text{m}$  syringe filters.

#### 2.4. Determination of elements in plant samples and soil

The contents of Fe, Mn, Cu, Zn, Ni, Cr, Cd, Pb, Sn, Co, Hg, and As in the samples were determined using inductively coupled plasma mass spectrometry (ICP-MS) (PQ ExCell, Thermo Elemental, UK) and P by an inductively coupled plasma atomic emission spectroscopy (ICP-AES) (JYULTIMA – 2, French). The calibration standards of ICP – MS and ICP – AES were prepared in 5% (v/v) nitric acid by dilution of multi-element stock standard solutions. The technique of internal standardization was used to eliminate possible non-spectral interferences and to correct temporal signal drift. The recovery rate for the GSV – 2 sample was between 80% and 120%. Ten percent of the samples were randomly selected for duplicate measurement, and the relative standard deviation of these measurements was lower than 5%, which was acceptable. The mean element concentrations of plant materials were reported in  $\text{mg}\cdot\text{kg}^{-1}$  based on dry weight. The contents of Fe, Mn, Cu, Zn, Ni, Cr, Cd, Pb, Sn, Co, and as were determined using inductively coupled plasma mass spectrometry (ICP – MS). Hg was determined by atomic fluorescence spectrometry (AFS), and P was determined by spectrophotometer (S-P).

### 3. Results

There were no regular variations for the elements of Mn, Fe, Cu, As, and Sn in the tree rings, and concentrations of Co, Ni, Cr, and Hg were below the detection limits in most of tree rings. Therefore, we will only present and discuss the results for the elements of P, Cd, Pb, and Zn.

#### 3.1. The distribution of elements in soils

The concentrations of the four elements (P, Cd, Pb, and Zn) in soils are shown in Table 1. The contents of the four elements in the soil of RJK were higher than those in other sampling points, indicating that the soil background values in RJK were higher. In addition, the concentrations of Cd in most of the soil samples were much higher than the natural background value, but for Pb and Zn, this occurred only at the sampling point of RJK (the natural background value of Cd, Pb and Zn were 0.20 mg/kg, 35.00 mg/kg and 100.00 mg/kg). P has no soil standard value in China at present.

#### 3.2. The distribution of elements in tree rings

The concentration of P in tree rings from the three sampling sites increased from heartwood to sapwood (Fig. 2). These results are quite similar to those found in previous research (Cheng et al., 2007; Liu et al., 2009a, 2009b). For Zn, the concentrations in rings of all trees increased after 2007 except HQC–A (Fig.3).

The Cd contents of JHC tree rings increased continuously, while in the JHC–P tree rings, it maintained at high concentration levels (Fig. 4). In RJK–A and HQC–A tree rings, Cd contents were either detected in trace amounts or not detected at all. In contrast, the concentrations of Cd in RJK–P tree rings decreased sharply to 0.25 mg/kg in 1997 from 4.46 mg/kg in 1981 (the highest value among all tree ring samples), and tended to be stable after 1997. The Cd in HQC–P tree rings fluctuated from 0.01 mg/kg to 0.19 mg/kg, which was not remarkably high (Fig.4).

The Pb contents of JHC–A and JHC–P varied between 0.10 mg/kg and 0.50 mg/kg (Fig. 5). Similarly, Pb contents in RJK–A and RJK–P were generally below 0.50 mg/kg except for a high peak value of 2.06 mg/kg in 1992 for RJK–P tree rings. The concentrations of Pb in HQC–A and HQC–P were higher during the 1980s–1990s, and decreased after that time (Fig.5).

#### 3.3. Correlation analysis

To determine if the elements were correlated with the width of the tree rings, a concentration-width matrix analysis was conducted for each disc (Table 2). The results showed that for most elements, there were no significant correlations between element concentration and tree ring width. It indicated that tree ring growth was influenced by the comprehensive factors including climate change, atmospheric pollutants and edaphic conditions (Lee et al., 2015), rather than the specific single element that our research involved.

### 4. Discussions

#### 4.1. The relationship of elemental concentrations in soil and in tree rings

There are three ways for chemical elements to get into trees: (1) absorption from the soil by roots, and deposition in the xylem when elements are transported upward; (2) absorption from the atmosphere by leaves, and then deposition in the xylem; and (3) direct deposition onto stem surfaces and transfer to the wood through lateral movement across the bark (Lepp, 1974; Baes and Mclaughlin, 1984; Watmough and Hutchinson, 2003). Though it was found that Pb and Zn concentrations in tree rings were linearly related with those in soils in the Qixiashan Forest Park, Jiangsu Province (Xu et al., 2014), the adsorption of elements by different species of trees was different in the same soil

**Table 1**

The concentrations (mg/kg) of the elements in soils.

Site layer	JHC				RJK				HQC			
	P	Zn	Cd	Pb	P	Zn	Cd	Pb	P	Zn	Cd	Pb
1 <sup>a</sup>	0.764	77.15	0.22	23.82	1.529	113.45	0.33	50.08	1.099	80.64	0.24	26.20
2 <sup>a</sup>	0.806	77.09	0.18	25.26	1.3	97.26	0.32	44.77	1.112	73.83	0.26	23.15
3 <sup>a</sup>	0.96	71.09	0.18	21.22	1.698	100.57	0.22	54.24	1.104	69.38	0.19	21.21
4 <sup>a</sup>	0.937	75.66	0.26	21.80	1.288	98.04	0.28	44.40	1.163	67.75	0.35	21.55

<sup>a</sup> Layer 1 is 0–10 cm, layer 2 is 10–20 cm, layer 3 is 20–30 cm, layer 4 is 30–40 cm in soil.

types (Wang et al., 2005), not to speak of different soils. Our results showed that the correlation of element concentrations in soil and in tree rings was not significant. This is probably because the soil contents were cumulative data, while the element concentrations in tree rings were yearly values affected by physiology, climate and other environmental factors. We further found that the environmental pollution in the steelwork region was more serious than that in the rural areas of Xi'an (Liu et al., 2009a). However, pollution in the soils only reflects many years of accumulation, whereas the tree rings can record the yearly element concentration and reveal the pollution history and the degree.

4.2. Environmental change reflected by element variability in tree rings

Under most conditions, the change of element concentrations in tree rings can directly reflect the change of element content in the growth environment.

(1) P and Zn

P is an essential nutrient for plant growth. It plays a very important role in metabolism and is more likely to accumulate in sapwoods with

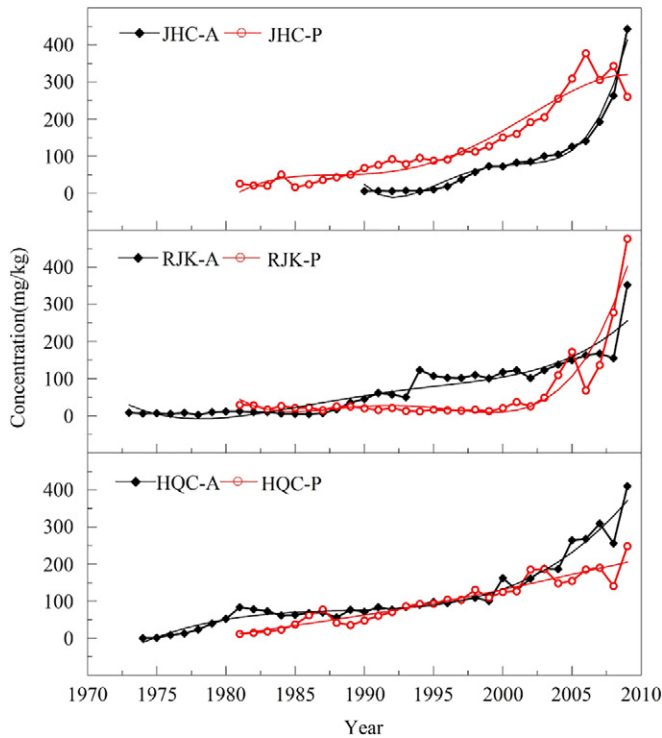
stronger metabolisms (Marschner, 1995; Rothpfeffer and Karlun, 2007). Most anthropogenic sources of P in the environment are detergents and phosphate fertilizers.

In fact, some studies considered that P was an outward mobility element in tree rings (Mcclenahan et al., 1989; Watmough and Hutchinson, 2002; Cheng et al., 2007; Biondi et al., 2008), as was also observed in our study. Inter-ring mobility of an element may obscure the pollution signal in tree rings and thus the concordance between environmental chemistry and dendrochemistry (Watmough et al., 1997). Therefore, the analysis of concentration variations of P in individual tree rings could not accurately reflect the environmental changes (Cutter and Guyette, 1993).

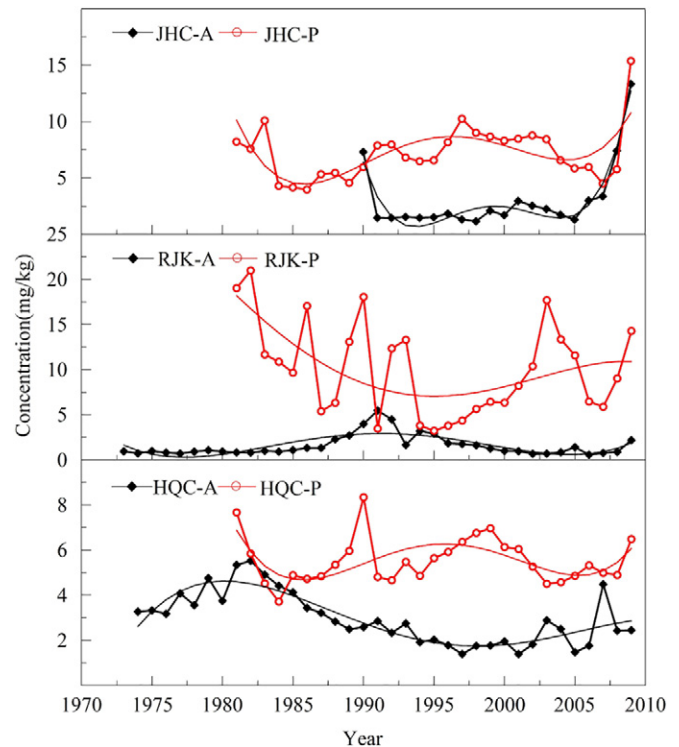
The major pollution sources of Zn in the environment are the wastes from lead zinc smelting, lead zinc mining, and galvanizing. There were no known emission sources around the three sampling sites, and the variations of Zn in tree rings appeared to be irregular. Previous studies reported that the concentration of Zn increased from heartwood to sapwood (Brackhage et al., 1996; Watmough, 1999). In our study, the concentrations of Zn increased in the outmost rings, so it might be caused by inter-ring migration.

(2) Cd

Cd is a highly toxic element. An outbreak of the itai-itai disease in Japan was caused by excessive Cd in paddy fields (Zhang, 1987). Cd is



**Fig. 2.** The radial distribution characteristics of phosphorus (P) element concentrations in tree rings. (JHC-A represents the ailanthus tree from Jiao Hua Chang, JHC-P represents the white poplar tree from Jiao Hua Chang, RJK-A represents the ailanthus tree from Ren Jia Kou, RJK-P represent white poplar tree from Ren Jia Kou, HQC-A represent ailanthus tree from Hong Qi Chang, and HQC-P represents the white poplar tree from Hong Qi Chang, similarly herein after).



**Fig. 3.** The radial distribution characteristics of Zinc (Zn) elemental concentration in tree rings.

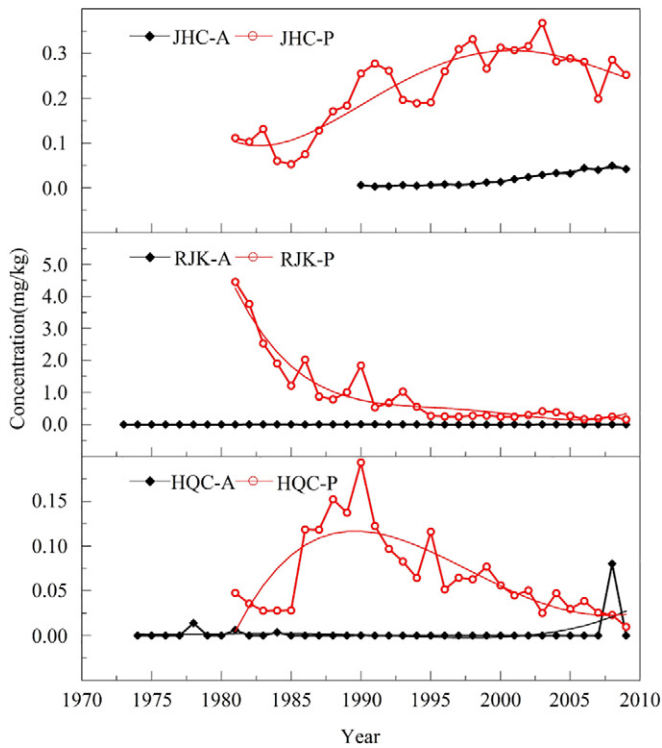


Fig. 4. The radial distribution characteristics of Cadmium (Cd) elemental concentration in tree rings.

stable chemically, so it is very difficult for it to degrade in soil. The anthropogenic sources of Cd in the environment are derived from waste water, waste gas and solid wastes discharged by industrial and agricultural activities.

Because of its accumulation and irreversibility, Cd discharged by the chemical plant in operation is continuously deposited and accumulated

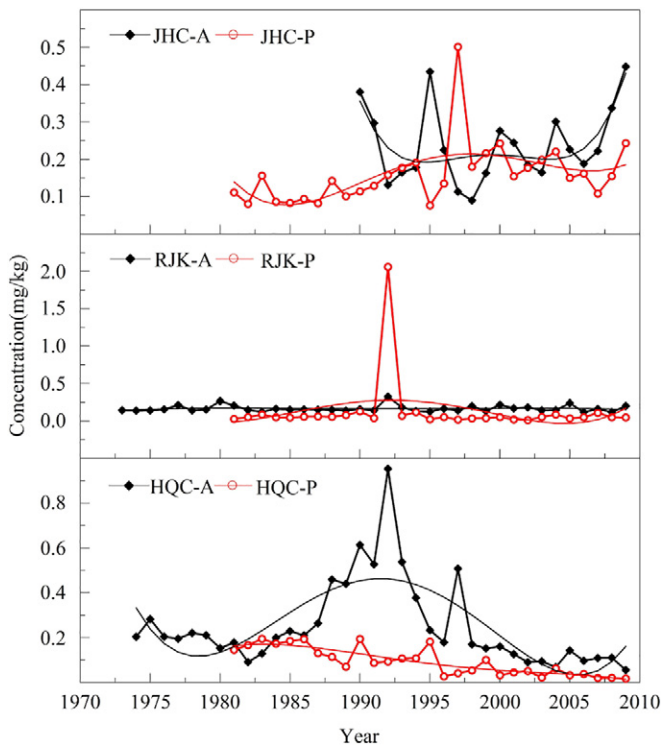


Fig. 5. The radial distribution characteristics of Lead (Pb) elemental concentration in tree rings.

Table 2  
Concentration-width correlation coefficient.

		Cd-wide	P-wide	Pb-wide	Zn-wide
JHC-A	Pearson correlation	-0.224	-0.299	-0.370	-0.551
	Sig(2 - tailed)	0.342	0.200	0.109	0.012
JHC-P	Pearson correlation	-0.279	0.254	-0.274	-0.072
	Sig(2 - tailed)	0.143	0.183	0.151	0.711
RJK-A	Pearson correlation	-0.421	-0.473	0.191	-0.268
	Sig(2 - tailed)	0.01	0.003	0.257	0.109
RJK-P	Pearson correlation	-0.026	-0.404	0.274	0.083
	Sig(2 - tailed)	0.895	0.030	0.150	0.667
HQC-A	Pearson correlation	0.063	-0.459	0.092	0.196
	Sig(2 - tailed)	0.713	0.005	0.593	0.252
HQC-P	Pearson correlation	0.195	-0.057	0.092	-0.179
	Sig(2 - tailed)	0.310	0.770	0.637	0.353

in the local environment, causing an obvious increasing of Cd concentration. Therefore, the Cd concentration in JHC-P tree rings maintained higher levels than trees from HQC with a low Cd pollution.

As shown in Fig. 4, Cd concentrations in RJK-P tree rings during 1981 to 1997 were much higher than for other tree samples, from up to ten times to dozens of times. Therefore, we believe that other Cd-release source(s) might exist. In fact, after investigation, a small sewage ditch flow past the location of the white poplar tree at the RJK site (Compilation committee of Xi'an chorography, 2000), indicating that the high concentrations of Cd could be the result of sewage irrigation. Variations of Cd concentrations in the RJK-P tree rings could, to some extent, reflect the changes of Cd in the surrounding environment (upstream region where the sewage flowed through in this study (Compilation committee of Xi'an chorography, 2000)). Specifically, Cd pollution in the sewage ditch was more serious before 1981 and was then gradually controlled and even disappeared around 1997. Moreover, the variations of contaminants could also be used to evaluate the effects or achievements in improving the environmental quality by means of industrial restructuring and pollution control.

### (3) Pb

Pb pollution in the environment comes mainly from coal, industrial waste, mining and gasoline. The major sources of Pb in the atmosphere are coal burning and automobile exhaust (Liu and Luo, 2009).

In this study, it was noted that Pb concentrations in tree rings of both JHC-A and JHC-P were still increasing after the chemical plant was shut down in 2007, indicating the presence of other pollution sources. There are many large industrial enterprises and main roads in this area, which contributed to the area industrial and traffic pollution here and made the concentration of Pb at this site the highest throughout Xi'an (Yin and Zhao, 2006; Han et al., 2008). Moreover, the variation of Pb concentrations at this sampling site was not notable; as the samples were affected by many factors, including human factors (factory operation, traffic flow) and environment factors (climate, rainfall, tree physiology).

Based on the statistical data, the amount of Pb discharged in Shaanxi province was the second most in 1992 during 1990 to 2009 (Wang and Guo, 2011), and as shown in Fig. 5, RJK-A and RJK-P trees caught the discharge event. Unleaded gasoline has been used widely in China since July 1, 2000 (Qin et al., 2010), while "unleaded" does not mean zero Pb in gasoline but rather with a Pb concentration below 0.013 g/L (He, 1998). Thus, Pb still exists in automobile exhaust. Statistics showed that the motor vehicle population in Xi'an City increased sharply from 2000 to 2009, from 261,960 to 982,270 vehicles (at an annual increase rate of 15.8%). The variation of Pb concentration in these two trees indicated that the Pb discharge did not decrease because of the increasing numbers of cars, and though the concentration of Pb in fuel oil was limited, this conclusion was similar to other studies (Gao et al., 2016).

According to the statistics, Xi'an used to be one of the ten most polluted cities in 1980–90s, and the coal cost was above 75% of primary

energy (Chen et al., 2003). The contamination in the atmosphere still gave priority to coal-smoke (Wu and Ma, 2001). Thus, the high Pb concentrations in HQC–A and HQC–P trees during this period recorded the environmental reality. To improve the quality of the atmosphere, environmental disposal engineering, such as “changing coal to gas”, was initiated in Xi’an, and natural gas was supplied since 1997. The decrease of Pb concentrations in the two trees from 1998 indicated that it was effective to control Pb pollution by reforming the fuel structure, improving emission structure and replacing decentralized heat-supply with centralized heat-supply.

Additionally, it was detected that in the same location, the contents of Cd and Zn in white poplar were higher than those in ailanthus, which indicated that the absorptive capacity of Cd and Zn by white poplar was stronger than that of ailanthus.

#### 4.3. The hysteresis and movement of elements

A certain amount of time must pass for an element to transfer from the soil to the roots (Erel et al., 1997; Puchelt et al., 1997; Whitehead et al., 1997; Ettler et al., 2004), which would lead to the lag of pollution time recorded by tree rings, the so-called “hysteresis”. Hysteresis means that the year when elements were found in tree rings may not be the year in which they were released to the environment (Bellis et al., 2004). Previous research has indicated that hysteresis could be attributed to lots of different factors, including physiological characteristics of different tree species, response patterns of trees to different elements, and soil conditions for the growth of trees (Cutter and Guyette, 1993; Smith and Shortle, 1996; Smith et al., 2008). In our research, hysteresis was reflected as follows: (1) although the chemical plant stopped production in 2007, the concentrations of Cd in JHC–A and JHC–P tree rings were still high in 2008; and (2) the highest Pb emission occurred in 1991 in Shaanxi province (Wang and Guo, 2011), while the peak value recorded by the RJK–A and RJK–P tree rings was found in 1992. Our results show that some elements migrate across tree rings. For example, P and Zn exhibit movement from heartwood to sapwood, which has been confirmed by many experiments. The movement of elements may cause reduction or loss of the accuracy of the pollution chronology.

#### 5. Conclusions

- (i) Considering the hysteresis of element, the variation of Cd and Pb concentration in tree rings could reflect historical changes of local air and soil quality. Therefore, these elements could be used as tracers for environmental pollution.
- (ii) Some elements are translocated across tree rings, such as P and Zn in this study. The movement may lead to variations of element concentrations in tree rings not accurately reflecting the pollution chronology in the environment. Therefore, when reconstructing the pollution history, it is necessary to choose suitable elements according to weight and therefore translocation process among tree rings.
- (iii) There was no good correlation between the element contents in soil and in tree rings because the absorption of elements by trees was affected by many factors.
- (iv) The capacity for absorption of a specific element by one tree species was stronger than another. For example, the absorptive capacity of white poplar to absorb Cd and Zn was stronger than for ailanthus. Our results can be used to advise the selection of tree species in environmental remediation projects.

The results presented here indicated that dendrochemistry has great potential in reflecting the history of environmental changes and particularly of air and soil quality. Dendrochemistry can help conventional

environmental monitoring which is limited to the past 2 or 3 decades in extending back in time over decades on soil and air quality.

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