Journal of Environmental Sciences Vol. 18, No. 5, pp. 916—920, 2006

ISSN 1001—0742
CN 11—2629/X

Article ID: 1001-0742(2006)05-0916-05 **CLC number**: X131.1 **Document code**: A

Acidity and conductivity of *Pinus massoniana* bark as indicators to atmospheric acid deposition in Guangdong, China

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Abstract: Barks of *Pinus massoniana* collected from two polluted sites, Qujiang and Xiqiaoshan, and from the relatively clean site Dinghushan were used to evaluate the pollution indication by the determination of their acidity and conductivity. The acidity of the inner and outer barks from the polluted sites was significantly higher than those from the clean site, suggesting that the acidity of the bark occurred in concurrent with the air pollution. The significant lower pH values of the outer bark than the inner bark collected from all sites indicated that the outer bark was more sensitive than the inner bark in response to acid pollution, implying that the outer bark is more preferable when used as indication of atmospheric acid pollution. The conductivities of the inner barks differed significantly among the three sites, with higher values at the clean site. However, the significant differences were not observed among these sites. Furthermore, the pH values for the inner and outer barks were not correlated with the conductivity, which did not coincide with some other studies.

Keywords: acidity; conductivity; inner bark; outer bark; *Pinus massoniana*

Introduction

The ever-increasing development of human activities has given significant rise to atmospheric pollutants which have negative impacts on natural ecosystems, as for example the severe decrease of the forests (Soikkeli, 1981; Hirano and Hijii, 1998; Grodzińska-Jurczak and Szarek-Łukaszewska, 1999; Muzika *et al.*, 2004; Shparyk and Parpan, 2004; Smidt and Herman, 2004). Sulphur dioxide and nitrogen oxides are known as major pollutants in industrial areas, primarily as causative agents of acid rain. Awareness of this environmental problem has led to the setting up of numerous organizations specializing in air quality evaluation (Bortnick and Stetzer, 2002). Assessing environmental pollution by using plants has been of increasing interest and proved to be a complementary method of investigation for pollutant analysis (Hawksworth and Rose, 1970; Seaward, 1993; Monna *et al.*, 1999; Alaimo *et al.*, 2000; Oliveira, 2000; Conti and Cecchetti, 2001). Higher plants have been used as bioindicator of particular pollutants in numerous studies (Kozlov *et al.*, 2002; Manning *et al.*, 2002; Klumpp *et al.*, 2003; Gravano *et al.*, 2003; Manning and Godzik, 2004; Nakatani *et al.*, 2004). However, tree barks were much less frequently used to indicate air pollution than tree foliage in the realm of the vascular plants even if their sensitivity to air pollutants has been praised (St äxang, 1969; Grodzińska, 1971, 1977, 1979; Lötschert and Köhm, 1977; Santamaría and Martín, 1997; Narewski *et al.*, 2000; Pacheco *et al.*, 2003). Grodzińska (1971) and Lötschert and Köhm (1977) revealed that tree bark was excellent material for determining the degree of environmental acidity due to gaseous sulphur dioxide pollution. In fact, several advantages by making tree bark as potential bioindicator to air pollution were praised. Firstly, tree barks are ubiquitous in nature and easily accessible. Secondly, they have large surface area continually exposed to atmosphere for tens of years which allowed relatively long-term pollution episode to be determined. Thirdly, they can be easily collected in field without highly trained staffs. Although decreased pH values have been reported in the tree barks from the high industrial activity area (Santamaria and Matin, 1997), a problem exists with interpretation of chemical data from the tree barks. Within the barks there are two parts outside the woody body according to the Satake *et al.* (1996). One is the living part, the inner bark, and the other is the dead part, outer bark. The relative importance of impacts of pollutant directly from the atmosphere compared with the impacts from the soil on the different parts may be neglected. Due to the small part of the inner bark, most previous studies except Satake *et al.* (1996) have sampled the whole bark for analysis, thereby ignored the difference between the two parts. In the present study, the inner and outer bark of Masson pine (*Pinus massoniana* L.) growing in the polluted and relatively clean environments, respectively, were used to evaluate the pollution indication by the determination of their acidity and conductivity.

Masson pine is a ubiquitous distribution tree species across subtropical China. It is highly sensitive to atmospheric acid deposition (Han and Liang, 2001), which makes it a good candidate for comprehensive surveys of air pollution. Guangdong Province, located in south China, has undergone increasing urbanization

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Foundation item: The National Natural Science Foundation of China (No. 30370283), the CAS Orientation Project (No. KSCX2-SW-120; KSCX2-SW-133) and the Natural Science Foundation of Guangdong Province (No. 04002306); * Corresponding author and industrial development in the last decades. Environmental pollution and ecosystem deterioration has been of an increase concern in these developing regions (Zhang, 1999). The increase of acid emission and deposition has caused significant negative impacts on local vegetations (Hu and Su, 1999; Luo *et al.*, 2001; Jin, 2002; Wen *et al.*, 2003) and acid rain has been considered the major environmental problem since 1980 (Jin, 2002). The purposes of the study were to (1) identify the characteristics of the pH value and conductivity of the inner and outer bark of Masson pines growing under different levels of pollution, and (2) determine the advantages and relative importance of different components of tree barks in air pollution monitoring. Due to the lack of similar investigations in the areas, we hope that the results from this study would provide preliminary information on the impact of acid deposition on the ecosystem.

1 Material and methods

1.1 Sites description and tree bark sampling

Masson pines growing at Qujiang of Shaoguan district and Xiqiaoshan of Foshan where were considered as polluted areas, and at Dinghushan reserve which is a relatively clean area, were chosen for tree bark sampling. All the studied sites were characterized by subtropical monsoon climate. The annual precipitation was within the range of 1600—1900 mm, which mainly distribute in the wet season from April to September. Shaoguan, one of the main smelting industry centers in Guangdong Province was influenced by emission from Pb-Zn smelting plant and power plants. According to Xie *et al.* (2002), Shaoguan and Guangzhou were the acidic center in Guangdong Province. Han and Liang (2001) reported the amount of SO_4^{2-} input from atmospheric deposition into the Masson pine forest located at Shaoguan reached 35.29 mol/(hm^2·a). In the last decade, the mean pH value of the rainfall was 4.45 and the frequency of acidic precipitation was above 70%. The mean value of SO_4^{2-}/NO_3^- in the rainfall was 13.8, which is the highest in the Pearl River Delta (Xie *et al.*, 2002). Foshan, one of the most rapidly developed areas, received large amount of pollutant emission from ceramic industries each year since 1990s. The frequency of acidic precipitation and the pH values of rainfall from 1988—2002 are shown in Fig.1. The mean value of SO_4^{2-}/NO_3^- in the rain fall reached 7.9 (Huang *et al.*, 2003). This implied that the air pollution at the two sites was mainly caused by the sulphur dioxide from the industrial emissions. For example, the total industrial emission of SO_2 in 1995 reached 72500 t at Shaoguan, 102800 t at Foshan, while at the reference site, Zhaoqing, the emission was only 5300 t, the deposition of S was 5.25 g/m^2 at Foshan, 1.62 g/m^2 at Zhaoqing (Xie *et al.*, 2002).

At the polluted sites, Masson pines within about 10 km away from the industrial center were selected for bark sampling. The control samples were taken from a Masson pine forest growing at Dinghushan reserve with the annual mean level of SO_2 lower than 0.02 mg/m^3. All the sample trees are about 40 years old.

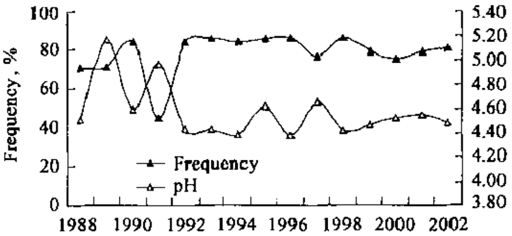

Fig.1 Frequency of acidic precipitation and pH values of rainfall during 1988—2002 at Foshan

In order to minimize possible effects of rainfall on sample collection, sampling was performed at stable weather conditions in November of 2002, and completed within two consecutive days. Twenty trees were selected for bark sampling at each site. Sample trees were healthy looking with the diameter above 40 cm and at least 100 m away from each other and 200 m away from the roads. The full bark was carefully removed from tree trunk at an average height of 1.5 m with a stainless steel knife. Prior to collection, mosses and lichens were removed with a synthetic hard brush. Bark samples were kept in a paper envelope and then placed in a polythene bag before transportation to the laboratory. To reduce the influence of orientation, an entire ring bark from each tree was sampled to constitute one sample.

1.2 Sample preparation

In the laboratory the bark were divided into the inner part and the outer part according to Satake *et al.* (1996) (Fig.2) with stainless steel knife. The separated samples were not washed because the aim of this study was to measure the acidic matters that were physically trapped on the surface of the bark. All samples were dried in the oven at a temperature of 105℃ for about 5 h to constant weight. Each sample was then pulverized to uniform size with a laboratory mill. The mill was thoroughly cleaned and dried after each grinding to avoid contamination.

1.3 Chemical analysis

Two grams of each dried sample was put into a 25-ml flask. 20 ml distilled and degasified water was added in each flask. All samples were shaken continuously for 48 h, the extract was used to measure the pH and conductivity by Microprocessor pH Meter (HANNA pH 211, Italy) and digital conductivity meter (DDS-11A, China) at room temperature (about 20℃), respectively.

1.4 Data analysis

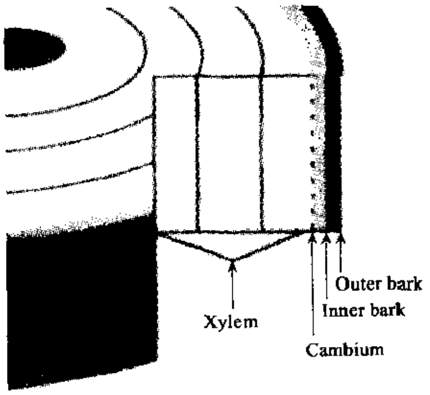

Fig.2 Diagram of the tree bark (Satake *et al.*, 1996)

ANOVA was used to determine the site effect (inner bark) and the air pollution effect (outer bark) on the pH and conductivity of the bark. The *t*-test was used to confirm the difference of the pH values and conductivity between the inner bark and outer bark among the sites. Linear relationships between the pH and conductivity of the inner and outer bark were investigated with Pearson test, too.

2 Results and discussion

2.1 Acidity of the bark

As shown in Fig.3 and Table 1, the mean pH of the inner bark from all sites was significantly higher (n=60, $p<0.01$) than that of the outer bark, indicating that the outer bark was influenced much higher than the inner bark and an acidification process may occur in the external tissues. We assume that this acidification is dominated by pollution deposition, not by microbiological process, since bark biodegradation is very slow in natural condition (Kilbertus, 1985).

The outer bark exposed directly to the atmosphere is permanently leached by stem-flow because of rainfall which is often acidified in heavily acid deposition area. In fact, tree bark functions as a cation exchange system decrease with no compensation because the outer part of bark is non-living. As a result, an acidification of the outer bark may link with the irreversible loss of buffering capacity. The outer tissues are exposed to more leaching and gradually lose their buffer capacity and showed more acid than the inner bark.

The pH values in the inner and outer bark from Dinghushan reserve were significantly higher than those from the polluted sites (Xiqiaoshan and Qujiang), but no statistical difference was observed between the inner and outer barks collected from polluted sites (Tables 1 and 2). This implied that the atmospheric pollutants may influence the acidification of the tree bark directly, which could be related to the atmospheric deposition of acidic matters including sulphur dioxide and nitrogen oxides. Samples from two polluted sites are near the industrial center, the pH values of the outer bark may decrease by industrial emission and accumulation of acidic matters when compared with those from the clean site, suggesting that the outer bark pH values were influenced by the pollutant emissions. The results verified the atmospheric monitoring result that the acidic deposition in Foshan and Shaoguan were higher than that in Zhaoqing (Zhang, 1999).

Pollutants can be introduced into the bark by two different ways-through the root system and the biological cycle of the tree or by accumulation processes from air and water onto the outer bark layer. In the majority of tree species, the tissues located outside the cambium layer evenly die due to the lack of water and minerals, the died tissue enlarged greatly the surface area and the roughness of tree barks, thus, lower acidity of outer bark could be explained by nature of Masson pine bark, which were rough and thick enough to accumulate pollutants from acidic deposition. Researches have confirmed that rough bark could accumulate pollutants more than smooth bark (Barnes *et al.*, 1976) and industrial activity tends to increase the concentration of contaminants of bark (Odukoya *et al.*, 2000). However, the inner bark surrounding the cambium, remains active preventing the formations of a thick bark. Therefore, the nutritional state of the inner bark has a direct influence on the pH values.

The acidities of the inner bark were negatively correlated with those of outer bark for all sites, indicated by the Pearson correlation analysis (r=

Table 1 Results of the bark pH values and conductivity from Dinghushan (DH), Xiqiaoshan (XQ) and Qujiang (QJ) by ANOVA

	Source of variances	Sum of square	*df*	Mean square	*F* value	Significance
Inner bark pH	Between sites	3.365	2	1.682	22.771	0.000
	Within site	4.211	57	0.074		
	Total	7.576	59			
Outer bark pH	Between sites	2.250	2	1.125	25.920	0.000
	Within site	2.474	57	0.043		
	Total	4.724	59			
Inner bark con.	Between sites	1011781.033	2	505890.52	39.056	0.000
	Within site	738318.90	57	12952.96		
	Total	1750099.9	59			
Outer bark con.	Between sites	59499.03	2	29749.52	1.710	0.190
	Within site	991719.90	57	17398.60		
	Total	1051218.9	59			

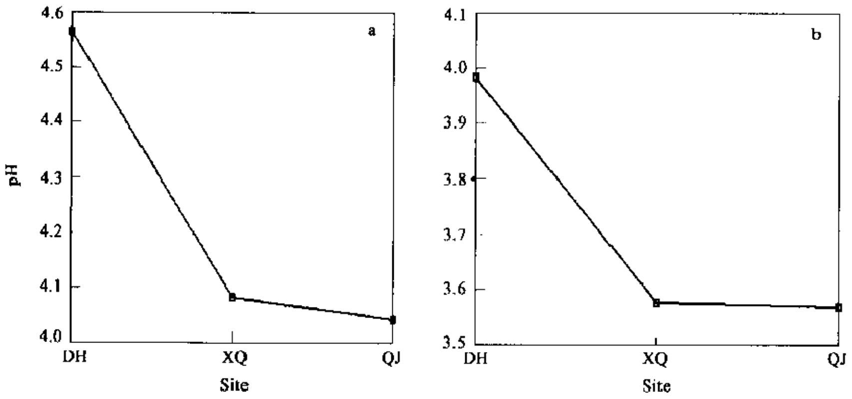

Fig.3 Comparison of pH values of the inner bark(a) and outer bark(b) from Dinghushan (DH), Xiqiaoshan (XQ) and Qujiang (QJ)

Table 2 Results of multiple comparisons of the inner and outer bark values from Dinghushan(DH), Xiqiaoshan (XQ) and Qujiang (QJ)

Value	Paired sampling sites		Mean difference
Inner bark pH	DH	XQ	0.4820^{**}
	DH	QJ	0.5205^{**}
	XQ	QJ	0.038
Outer bark pH	DH	XQ	0.4065^{**}
	DH	QJ	0.450^{**}
	XQ	QJ	0.0085
Inner bark con.	DH	XQ	175.45^{**}
	DH	QJ	317.50^{**}
	XQ	QJ	142.05^{**}
Outer bark con.	DH	XQ	-75.55
	DH	QJ	-51.25
	XQ	QJ	24.30

Note: The mean difference is significant at the 0.01 level

-0.427, -0.558, -0.477 for Qujiang, Xiqiaoshan and Dinghushan, respectively, $p<0.01$).

2.2 Conductivity of the bark

Conductivities of the inner bark from all the sites were significantly higher than those of the outer bark (Fig.4). According to Garrec *et al.* (1989), the cambial electrical resistance (opposite to conductivity) depends essentially on the presence of mobile ions, which were mainly absorbed by roots could partially transit from xylem to phloem and even to bark (Walkenhorst *et al.*, 1993). At the inner part, the bark is still a young and thin tissue and consequently is rich in cations, which increased the conductivity. When the bark is thick and older, the outer part is gradually leached by stem-flow and loses its cations (Farmer *et al.*, 1991). Thus the conductivities were decreased. The significantly difference of the inner bark conductivities among different sites may be related to the inner vigor of the trees and the difference of cation level caused by the deposition of air-born pollutants, since the inner conductivities from the clean site were statistically higher than those from the polluted sites, but no statistical difference of the outer bark conductivities were observed between different sites (Table 2). Therefore, we suggested that the conductivity of the inner bark may be more effective to indicate the environment than the outer bark.

2.3 Correlation between the acidity and the conductivity

The analysis of correlations between the pH values and conductivity will allow further qualification of this measurement. We found that pH values are not correlated with conductivity neither for inner bark nor for outer bark from all the sites, which agreed with the result in silver fir (*Abies pectinata*) (Legrand *et al.*, 1996). Bark includes all external tissues of the vascular plants, so it is more probable that conductivity are directly or indirectly and strongly influenced by the compositive factors such as the ions in the internal tissues (functional phloem, cambium and young xylem), the physical structure of the bark, the acidity, the environments.

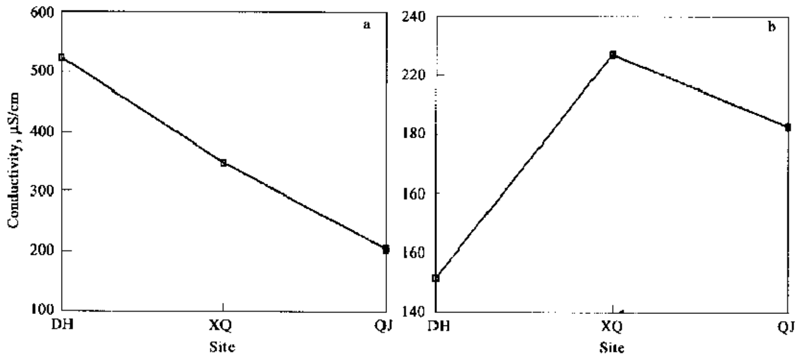

Fig.4 Conductivity of the inner bark (a) and outer bark (b) from Dinghushan (DH), Xiqiaoshan (XQ) and Qujiang (QJ)

3 Conclusions

The present results suggested that the acidity of Masson pine bark, especially its outer parts, can be used to evaluate air conditions on a certain scale. Analysis of bark acidity can provide a basic and simple determination on a long-term impact of pollution, and give an early warning signal of modifications in environmental quality. The impacts of air pollution on the conductivity of the outer bark were not as obvious as that on the inner bark. The inner conductivity may be more useful to indicate environmental pollution than the outer one. Further study to confirm the possible influence of atmospheric pollution on Masson pine widespread in south China and to assess the regional-scale air quality should be necessary.

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(Received for review October 25, 2005. Accepted March 6, 2006)