

POROSITY AND PORE SIZE DISTRIBUTION OF RECENT AND ANCIENT BURIED *PHOEBE ZHENNAN* WOOD DETERMINED BY MERCURY INTRUSION POROSIMETRY

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ABSTRACT

The porosity and pore size distribution of recent and ancient buried *Phoebe zhennan* are studied in this paper by means of mercury intrusion porosimetry. The results show that the micropore and mesopore diameters of recent and buried wood are mainly distributed in range of 40.3 nm and 183.1 nm respectively, while the macropore in 45276.6 nm and 3503.9 nm separately. For both samples, the pores with diameters below 349.9 nm account for about 60% of the total intrusion volume, and contribute more than 98% of the surface area. The cumulative pore area of recent wood is slightly greater and the pore diameter ranges from 50.3 nm to 349.9 nm. While the cumulative pore area of buried wood is significantly larger than and the pore diameter ranges until 50.3 nm. These results can provide information for further investigations on the sorption behaviour and the liquid permeability of ancient buried wood.

KEYWORDS: Porosity, pore structure, *Phoebe zhennan*, ancient buried wood, mercury intrusion porosimetry.

INTRODUCTION

Buried wood refers to dead wood that is more than 50% buried by soil, garbage or ground vegetation through natural disasters such as landslides and river deposits or through excessive growth of ground vegetation (Jianyi et al. 2019, Moroni et al. 2015). The buried wood often persists many centuries (Boutelje and Bravery1968, Kim 1987, 1990) or even thousands of years (Hedges et al. 1985, Hoffmann et al. 1986, Liyama et al. 1988, Meyers et al. 1980).

The process of wood burial appears to occur mainly through two mechanisms (Moroni 2015), rapid burial through catastrophic events such as landslides and fluvial deposition (Eden 1967) or gradual burial of downed deadwood through litter deposition and overgrowth by ground vegetation (Dynesius et al. 2010, Hagemann et al. 2010a, Moroni et al. 2010). Buried wood has different physical and chemical property from that of recently cut wood. The effect of time on the buried wood caused hemicelluloses degradation and a decrease in the crystallinity index and the crystallite length, resulting in an increase in the proportion of amorphous zones (Esteban et al. 2006). Because of this, the equilibrium moisture contents of the buried wood are higher than of the recent wood, both in adsorption and desorption (Esteban et al. 2008). In terms of the thermodynamic properties, the heat involved is greater in the buried wood than in the recent wood (Esteban et al. 2009).

Buried *Phoebe zhenan* (family: Lauraceae, category: *Phoebe*) wood is precious for its beautiful color and pattern, light fragrance, and is widely used in costly furniture manufacturing, handicraft carving and other fields. However, the ancient buried *P. zhenan* wood is hard to dry and easy to crack, which affects its processing and utilization. The deformation and drying characteristics of buried wood are related to its internal structural characteristics, especially the porosity and pore size distribution. At present, the researches on pore size distribution of wood and wood-based products by mercury intrusion porosimetry are studied (Zauer et al. 2014, Pfriend et al. 2009, Plötze and Niemz 2011, Gigac et al. 2017). But the study on the pore characteristics of ancient buried wood is rarely reported. The aim of this research is to study porosity and pore size distribution of recent and ancient buried *P. zhenan*, which can provide useful information, particularly on the liquid permeability, and supply technological characteristics in its industrial processing.

MATERIAL AND METHODS

Recent and ancient buried *P. zhenan* were both provided by a wood company located in Chengdu, Sichuan Province, China. The samples were obtained from an 80-year old *P. zhenan* tree that had been buried for approximately 1500 years, dating by means of conventional radiocarbon, Carbon-14 (14C), radiocarbon dating. Recent samples were obtained from an 86-year old living tree. Both wood samples were placed in room temperature about 20°C conditions for air drying.

Mercury intrusion porosimetry

Porosity and pore size distribution of wood were tested by mercury injection apparatus (AutoPore IV 9500). The samples, with dimensions of 20 × 10 × 10 mm (longitudinal × tangential × radial), were cut by scroll saw from both woods.

Samples were immersed in non-wetting mercury, and measurements were then conducted by two processes of low and high pressure to increase the pressure steadily from 0 to 400 MPa. Mercury progressively intruded into smaller voids under the increased pressure. The pore volume could then be derived from the quantity of the intruded mercury. The pore size distribution can be determined according to Eq. 1 (Washburn 1921):

$$d = - \frac{4\gamma\cos\theta}{p} \quad (1)$$

where: d - pore diameter, p - pressure, γ - surface tension of mercury (0.48 N.m-1), θ - wetting angle of mercury (141°) (Junghans et al. 2005).

RESULTS AND DISCUSSION

The results of the mercury intrusion porosimetry measurements for recent and ancient buried *P. zbennan* samples are showed in Tab. 1.

Tab. 1: Mercury intrusion porosimetry test results of recent and ancient buried *P. zbennan* samples.

<i>Phoebe zbennan</i>	Total intrusion volume (mL·g ⁻¹)	Total pore area (m ² ·g ⁻¹)	Median pore diameter (volume) (nm)	Median pore diameter (area) (nm)	Average pore diameter (4V/A) (nm)	Bulk density at 0.43 psia (g·cm ⁻³)	Porosity (%)
Ancient buried <i>P. zbennan</i>	1.0909	65.44	113.7	34.7	66.7	0.521	56.812
Recent <i>P. zbennan</i>	0.9678	25.95	255.2	55.2	149.2	0.577	55.841

The bulk density (at 0.43 psia) of the buried wood is lower than that of the recent, which may be due to the degradation of cellulose and hemicellulose, so the porosity and total intrusion volume of buried wood are larger (Schniewind 1990). However, the median pore diameter (volume), median pore diameter (area), average pore diameter (4 V/A) of the buried wood are significant lower, indicating that most of the pore in the buried wood is smaller, which caused the total pore area of buried wood is more than 2.5 times larger than that of the recent wood.

Log differential intrusion versus pore diameter of recent and ancient buried *P. zbennan* are showed in Fig. 1. According to the pore size distribution, four pore size classes could be distinguished: macropores (58 μm - 0.5 μm), mesopores (500 nm - 80 nm), and micropores (80 nm - 1.8 nm) (Plötze and Niemz 2011). There are two obvious peaks of recent *P. zbennan*, and the corresponding pore diameter of the two peaks are 45376.6 nm and 183.1 nm. The pore structure of vary structural in hardwoods are showed in Tab. 2 (Butterfield 2006, Stamm 1972, Stamm 1967). It can be seen from the data in the Tab. 2, the pore with diameter of 45376.6 nm is mainly from vessels, while the pore with diameter of 183.1 nm are mainly from pit membranes of bordered pits. Compared with recent *P. zbennan*, the peak of ancient buried *P. zbennan* moves in the direction of small pore diameter and the corresponding pore diameter of vessels are 3503.9 nm and 7244.9 nm, which due to the cell wall of buried wood were obviously compressed and more natural mineral deposits were deposited inside the vessels cavities of the buried wood (Jianyi et al. 2019). The pore diameter of ancient buried *P. zbennan* microcapillary (vessels, cavities of fibers, pit chamber apertures, pit apertures) are smaller than that of the recent *P. zbennan*, which reduces the gas and liquid permeability of the ancient buried *P. zbennan*, and results in water movement, adhesive penetration in ancient buried *P. zbennan* wood difficult. The corresponding pore diameter of pit membranes is 40.3 nm, which due to pit membranes were blocked by natural mineral deposits adhered in cell wall of the buried wood.

Tab. 2: Pore structure in hardwoods.

Structural elements	Diameter	Pore shape
Vessels	20 ~ 400 μm	Tubular
Cavities of fibers	10 ~ 15 μm	Tubular
Pit chamber apertures of bordered pits	4 ~ 30 μm	Ink bottle-like
Pit apertures of bordered pits	400 nm ~ 6 μm	Tubular
Pit membranes of bordered pits	10 nm ~ 8 μm	Polygonous spaces
Cell wall (dried)	2 ~ 100 nm	Slite-like, cylindric, slite-like and cylindric

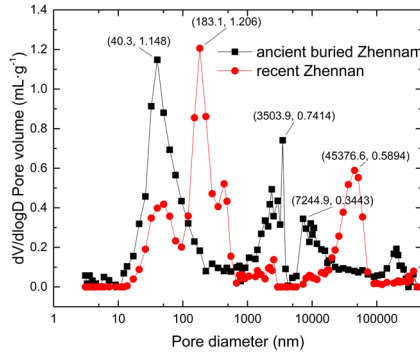


Fig. 1: Log differential intrusion versus pore diameter of recent and ancient buried *P. zhennan*.

Fig. 2 and Fig. 3 show the cumulative pore volume (CPV) and percentage of intrusion volume (PIV) versus pore diameter of recent and ancient buried *P. zhennan*. Fig. 2 indicates that the CPV and PIV of recent *P. zhennan* is greater than that of ancient buried *P. zhennan* in the pore diameter range from 3224.5 nm to 60385.8 nm, which are mainly from vessels, cavities of fibers, pit chamber apertures, pit apertures from the data shown in Tab. 1, and it shows a similar phenomenon in Fig. 3 for the increase of percentage of intrusion volume.

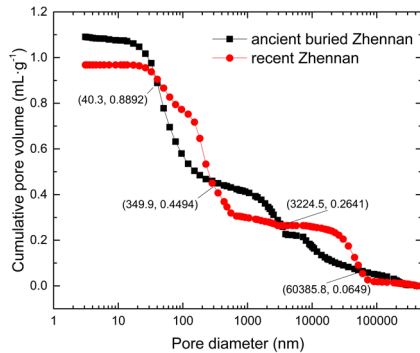


Fig. 2: Cumulative pore volume versus pore diameter of recent and ancient buried *P. zhennan*.

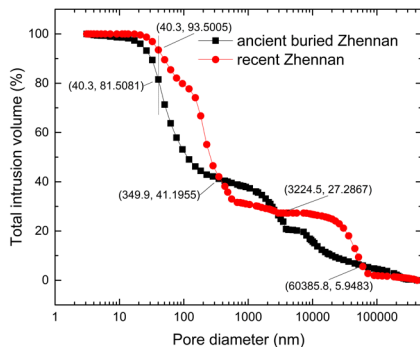


Fig. 3: Percentage of intrusion volume versus pore diameter of recent and ancient buried *P. zhennan*.

The reason is the cell wall of buried wood were obviously compressed and more natural mineral deposits were deposited inside the vessels and fibers cavities of the buried wood, blocking the vessels, cavities of fibers, pit chamber apertures and pit apertures (Jianyi et al. 2019). The compression of cell wall and deposition of the natural mineral lead to the pore diameter range from 349.9 nm to 3224.5 nm of ancient buried *P. zhennan* is more than that of the recent *P. zhennan*, so the CPV and PIV of recent *P. zhennan* is less than that of ancient buried *P. zhennan* in the pore diameter range from 349.9 nm to 3224.5 nm. The pore diameters range from 40.3 nm to 349.9 nm are mainly from pit membranes, the pit membranes of ancient buried *P. zhennan* were blocked by natural mineral deposits, so the CPV and PIV of ancient buried *P. zhennan* in this pore diameter range is less than that of recent *P. zhennan*. The pore diameters less than 40.3 nm are micropores in cell wall, the CPV and PIV of recent *P. zhennan* is more than that of ancient buried *P. zhennan* in this pore diameter range. This due to the microstructure of buried wood is destroyed after the transformation of the natural environment, causing a small amount of cellulose or hemicellulose to be degraded, which leads to the micropores in the cell wall of buried wood is more than that of the recent one (Jianyi et al. 2019).

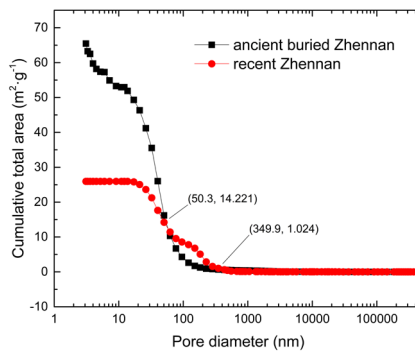


Fig. 4: Cumulative pore area versus pore diameter of recent and ancient buried *P. zhennan*.

Fig. 4 shows the cumulative pore area versus pore diameter of recent and ancient buried *P. zhennan*. It can be known from Fig. 3 and Fig. 4, for both recent ancient buried *P. zhennan* samples, the pores with diameters below 349.9 nm account for about 60% of the total intrusion volume, and contribute more than 98% of the surface area, while the pores with diameters above 349.9 nm account for about 40% of the total intrusion volume, and contribute less than 2% of the surface area. This can be explained by the surface area of micropores is much larger than that of macropores with the same volume. According to the log differential intrusion versus pore diameter of recent and ancient buried *P. zhennan* in Fig. 1, the micropore diameter of recent and ancient buried *P. zhennan* are distributed in 40.3 nm and 183.1 nm respectively, so the cumulative pore area of recent *P. zhennan* is slightly greater than that of ancient buried *P. zhennan* in the pore diameter range from 50.3 nm to 349.9 nm, while the cumulative pore area of ancient buried *P. zhennan* is significantly larger than that of recent *P. zhennan* in the pore diameter range below 50.3 nm, which proved that the degradation of cellulose or hemicellulose leading to the micropores in the cell wall of buried wood is more than that of the recent one.

CONCLUSIONS

The bulk density (at 0.43 psia) of the ancient buried *Phoebe zhenan* is slightly lower than that of the recent *P. zhenan*, while the porosity and total intrusion volume of ancient buried *P. zhenan* are a little larger. However, the median pore diameter (volume), median pore diameter (area), average pore diameter (4V/A) of the ancient buried *P. zhenan* are significantly lower than that of the recent *P. zhenan*, which caused the total pore area of ancient buried *P. zhenan* is more than 2.5 times than that of the recent *P. zhenan*. The micropore diameter of recent and ancient buried *P. zhenan* are main distributed in 40.3 nm and 183.1 nm respectively, while the macropore are main distributed in 45276.6 nm and 3503.9 nm separately. The pore diameter of ancient buried *P. zhenan* macrocapillary is smaller than the that of the recent *P. zhenan*, while pore diameter of ancient buried *P. zhenan* microcapillary is bigger than that of the recent *P. zhenan*. For both recent and ancient buried *P. zhenan* samples, the pores with diameters below 349.9 nm account for about 60% of the total intrusion volume, and contribute more than 98% of the surface area. The cumulative pore area of recent *P. zhenan* is slightly greater than that of ancient buried *P. zhenan* in the pore diameter range from 50.3 nm to 349.9 nm, while the cumulative pore area of ancient buried *P. zhenan* is significantly larger than that of recent *P. zhenan* in the pore diameter range below 50.3 nm.

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