Climate-affected Multi-decadal Variations of Biogenic Volatile Organic Compounds in *Pinus tabuliformis* Growth Rings

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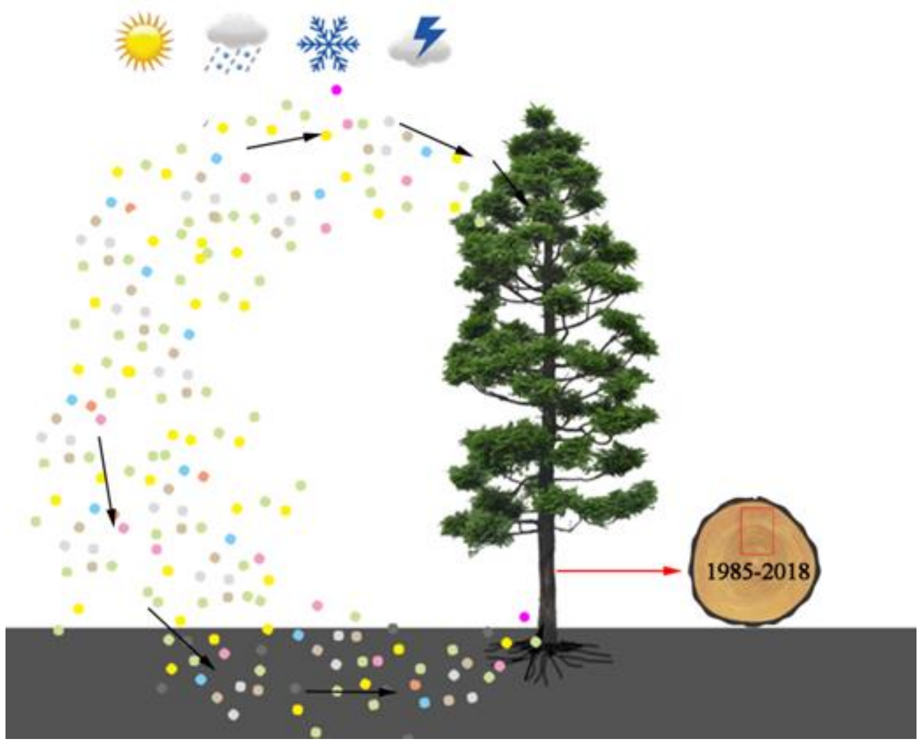
GRAPHICAL ABSTRACT



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Long-term dynamics of biogenic volatile organic compounds (BVOCs) in trees are rarely reported, despite environmental factors (such as climate change) influencing their growth and the subsequent chemical accumulation. For this, tree growth rings provide a promising biological proxy for the long-time variation and correlation with environmental changes. Therefore, tree rings from *Pinus tabuliformis* (two stem disks and 40 tree cores) were collected in the Taihang Mountain Macaque National Nature Reserve of China. These samples were divided into seven 5-year resolutions over the 34-year period 1985 to 2018. This enabled analysis of multi-decadal variations of compounds and their correlation with climate variability. A total of 292 BVOCs were detected; however, only 18 compounds were found together across all the 7 growth-periods. Temporal analyses showed decreasing trends for monoterpenes (0.026%/yr) and diterpenes (0.120%/yr), whereas alcohols and oxygenated monoterpenes showed increasing trends at 0.031%/yr and 0.042%/yr, respectively. Correlation analyses showed no obvious link to yearly precipitation, while seasonal temperature had a negative effect on monoterpenes and diterpenes but positive effects on alcohols and oxygenated monoterpenes (all $P < 0.05$). The present study showed that dendrochronology is a suitable method for re-establishing the biological effects from historical climate variability on key tree species.

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Keywords: Terpenes; Diterpenes; Alcohols; Tree ring; Climate change; Forest ecosystem services

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INTRODUCTION

Biogenic volatile organic compounds (BVOCs), emitted by vegetation into the atmosphere, have a large impact on atmospheric composition and air quality on both regional and global scales (Chen *et al*. 2020). In some broad-leaved species (such as *Quercus ilex*, *Fagus sylvatica*, and *Hevea brasiliensis*), emission of some BVOCs take place directly after its production, without intermediate storage within the leaf (Dindorf *et al*. 2006; Wang *et al*. 2007). Several recent studies suggest that short-term emission of BVOCs from woody species are affected by temperature (Chen *et al*. 2019, 2020; Wang *et al*. 2023). Diurnal and seasonal data show that both isoprene and monoterpene emissions increase with increasing temperature for both coniferous and broadleaved species, which reveal how BVOC emission rates are affected by temperature (Chen *et al*. 2019, 2020; Ge *et al*. 2020). Some studies also concluded that the constituents and emission magnitudes of BVOCs and diversification of chemical constituents depend on the age of tree species. Thus, age-dependent research is important to understand and conduct environmental studies (Waliszewska *et al*. 2015; Cardoso *et al*. 2018; Vermeuel *et al*. 2023). One study on seasonal emissions of two oak tree species (*Quercus aliena* and *Quercus mongolica*) showed that younger trees have significantly higher isoprene emission rates than those older ones (Lim *et al*. 2011). When the seasonal emissions from *Chamaecyparis formosensis* of different ages were compared, higher total emissions were also seen in saplings during cold seasons and adult trees during warm seasons (Chen *et al*. 2019).

Several other studies considered that some BVOCs (*e.g.* isoprene) are released immediately after the synthesis, and others (*e.g.* monoterpenes) stored in specialist structures in which emissions are affected by warming and age (Margarita *et al*. 2013; Kivimäenpää *et al*. 2022). Some previous studies confirmed that monoterpenes and other less volatile compounds can be stored in cellular liquid in leaves (Niinemets *et al*. 2002), or in specific storage organs such as resin ducts, resin canals (Niinemets *et al*. 2004; Margarita *et al*. 2013; Peng *et al*. 2020; Kivimäenpää *et al*. 2022), and glandular trichomes (Turner *et al*. 2000). The release of stored monoterpenes of many species is mainly determined by temperature. An algorithm was developed for estimating emission of monoterpenes on leaf or canopy scale (Holzinger *et al*. 2006), and on global scale (Mu *et al*. 2022). Because global warming affects temperature-dependent ecosystem processes in forests (Parks *et al*. 2023), the measures of nutrient availability and diversity of plant secondary compounds, including BVOCs, are becoming increasingly important. The biomonitoring on dynamics of BVOCs is important to understand the change of ecosystems and climate (Chen *et al*. 2019; Wang *et al*. 2023). The BVOCs studies are primarily concentrated on diurnal and seasonal emissions (Chen *et al*. 2019, 2020; Ge *et al*. 2020). Annual dynamics in monoterpene emissions are calculated by seasonal emission on a local scale (Schurgers *et al*. 2009). However, little is known whether there are some long-series BVOCs stored in long-lived tree species and how they change with climate and age. Thus long-term proxy data are needed to assess the emission and storage of BVOCs in long-lived trees. It can be hypothesized that the storage of BVOCs in wood with the passage of time may increase or decrease, depending on the influences of tree age, climate, and other factors such as environmental stress.

Environmental factors, such as temperature and precipitation, influence tree growth. Dendrochronology can re-establish air pollution, secondary compounds and plant biomass as a function of climate variability (Fritts 1976; Moullec *et al*. 2018; Hember *et al*. 2019; Khoo *et al*. 2020). Some information from tree rings has long been acknowledged for eco-physiological reconstruction of long-term climatic change (Cook *et al*. 1991; Grudd *et al*. 2002; Schurman *et al*. 2019) and for wood-chemistry physiology (Khoo *et al*. 2020) of long-time environmental pollution with heavy metals (Locosselli *et al*. 2018; Neto *et al*. 2023). Thus, the comparisons of chemical profiles in growth rings are helpful to allow study of the long-term temporal variations of chemical constituents in long-lived species. Moreover, some BVOCs from trees are important precursors for the generation of ozone (O_3) and secondary organic aerosols (SOA) that directly affect air quality (Ge *et al*. 2020). In contrast, several forest BVOCs (especially pinene and limonene) can also be significant sources of forest health and wellness by reducing mental fatigue, relieving anxiety, and promoting relaxation (Barbieri *et al*. 2020). Many studies have confirmed the long-time series climatic and ecological memory from tree ring data (Fritts 1976; Peltier *et al*. 2022). However, little is known whether there is long-term memory about chemical composition stored in tree special organs. Therefore, BVOCs stored in tree ring response to climate warming is essential to forecast the impacts of rising temperatures on wood compounds availability and hence improve understanding the effects of global change on future BVOC emission and forest ecosystem services (Yuan *et al.* 2017).

Chinese pine (*Pinus tabuliformis*) is an endemic coniferous tree species with a wide natural distribution in northern China, reaching the southern limit of its natural range to Qinling Mountains. The Taihang Mountain is the transition zone from warm temperate zone to north subtropical zone (Yu *et al*. 2023). Studying tree growth dynamics of *P. tabuliformis* in the Taihang Mountain not only can help to understand the growth response with climate warming, but also can enable corresponding predictions about their future change trends. Apart from some studies focusing on climate variability and tree-ring width (Liu *et al*. 2013; Duan *et al*. 2016), only limited information of emission from needles of *P. tabuliformis* is available in the literature (Chen *et al*. 2019, 2020). It is a main afforestation species in China, hence it is important to know its relative dynamics of BVOCs concentration and its correlation with climatic change. Therefore, the chemical contents with annual growth rings over multiple decades were studied. The objectives of this study were to: (1) assess the variation of BVOCs stored in tree rings, (2) investigate BVOCs trend along growth stages, (3) study the climatic influence on BVOCs, and (4) analyze the relationships among different BVOCs.

EXPERIMENTAL

Plant Materials Collection and Preparation

Pinus tabuliformis is a long-lived, shade-intolerant conifer, which mixes with *Quercus acutissima* in the Taihang Mountains. In the summer of 2019, two stem disks were sampled from fallen *P. tabuliformis* trees and 40 tree cores sampled from living *P. tabuliformis* trees (two cores per tree) in Taihang Mountain Macaque National Nature Reserve of China (35°250′ N, 113°11′ E). Climate data were obtained from the nearest Jiaozuo meteorological station (35°13′ N, 113°14′ E) including the monthly mean temperature and total precipitation.

The disks and core specimens were sanded and polished to enhance the visibility of ring width structure. To determine the year of each growth ring, tree rings from stem disks and tree cores were dated by COFECHA software (Rinntech, 1.0, Heidelberg, Germany) and one previous tree-ring width chronology of *P. tabuliformis* in this study zone (Peng *et al*. 2012). Then, the annual ring of disks was cut with a carving knife for investigation into the variation of BOVCs in growth rings with increasing age. To have enough samples for further experiments on each growth stages, all the accurate dated subsample wood chips were divided into seven 5-year periods: Y1 (1986 to 1989), Y2 (1990 to 1994), Y3 (1995 to 1999), Y4 (2000 to 2004), Y5 (2005 to 2009), Y6 (2010 to 2014), and Y7 (2015 to 2018). Each sample was ground to powder with an electric blender prior to extraction and then weighed as 10 g (accuracy was 1.0 mg) for the thermos-desorption (TD)-gas chromatography (GC)/mass spectrometry (MS) analysis (Staudt *et al*. 1997).

Thermo-Desorption GC/MS Analysis

TDS: The initial temperature was 30 °C, which was held for 1 min, then increased at 10 °C /min to 100 °C, retained for 5 min, and then raised at 10 °C /min to 230 °C. The transmission line temperature was 230 °C.

GC: The quartz capillary column used was HP-5MS (60 m × 0.25 mm × 0.25 μm), starting at 40 °C without retention, followed by a rate of 8 °C /min up to 250 °C without retention, and then finally at a rate of 5 °C /min to 280 °C, without retention. The column flow was 1 mL/min, and carrier gas was helium.

MS: The ionization mode was EI, the electron energy was 70 eV, the temperature of ion was 230 °C, the temperature of quadrupole was 150 °C, the quality range was 30 to 600 *m*/*z*, and the wiley7n.1 standard spectrum and computer search qualitative were used (Peng *et al*. 2011).

Climate-Chemical Components Associations

Monthly mean temperature and total precipitation were selected from the nearest Jiaozuo meteorological station built in 1961 in this area. The temperature and precipitation data were calculated into seasonal elements and then divided with a 5-year resolution to analyze the possible influence factors on long-term variation of stored BVOCs from tree rings of *P. tabuliformis*.

Statistical Analysis

Initially, data were checked and transformed to meet the requirements for parametric analyses. First, the Mann-Kendall test was used to evaluate the significance of the temporal trends of BVOCs from tree rings throughout the full growth stages (1985to 2018) of *P. tabuliformis* tree. Then, correlation between BVOCs and climatic factors were used to discuss climatic influence on BVOCs concentration. The correlation matrix and Spearman P-values were also employed to determine the relationships between the mean trends of individual BVOC throughout the study period 1985 to 2018. All statistical tests were computed using R statistical software (Lucent Technologies, 4.3.2, Paris, France) and value of significance was set to $P < 0.05$.

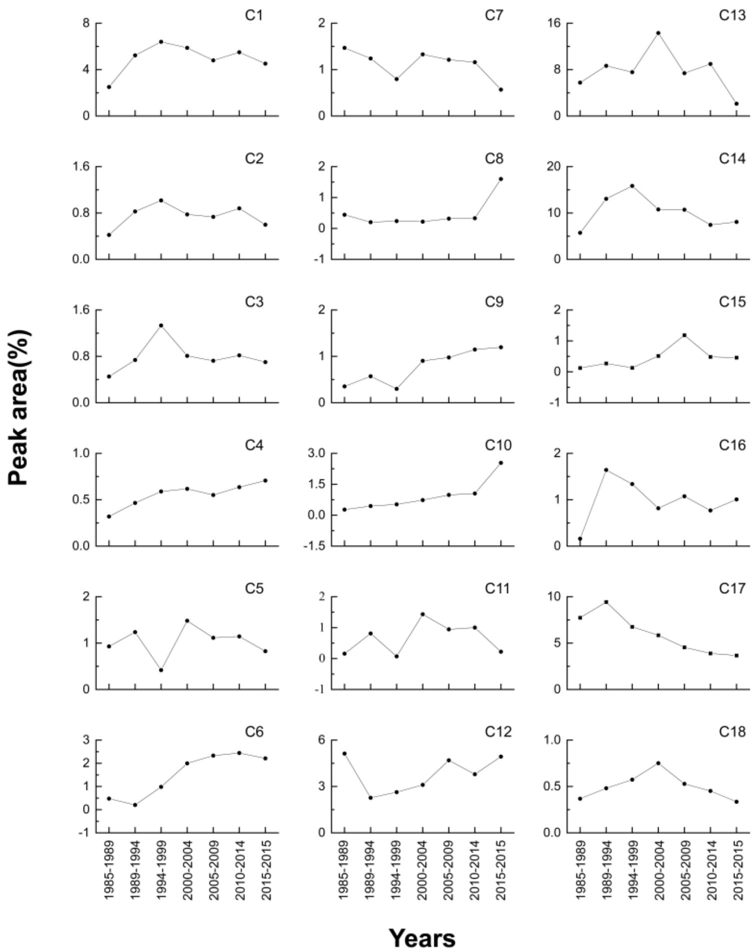
RESULTS

Chemical Components in *P. tabuliformis* Tree Rings

The BVOCs from every 5-year-growth period were extracted. The total number of extractive BVOCs reached 292 from tree rings of *P. tabuliformis* throughout all the seven growth periods. The number of BVOCs accounted for 95, 116, 117, 112, 99, 113, and 115 in the seven different periods Y1 to Y7, respectively (Table 1). Among the tree rings of *P. tabuliformis*, different periods shared similar BVOC profiles. The number of the same BVOCs ranged from a minimum of 41 (Y1 *vs*. Y3) to a maximum of 73 (Y2 *vs*. Y4), accounting for 35% to 65% of the total number in the respective periods (Table 1). Compared with a total of 292 extractive BVOCs in the 3.5 decades between 1985 and 2018, only 18 of the same compounds were found throughout the seven growth stages. The 18 most common BVOCs showed different concentration trends along increasing growth periods (Fig. 1).

Table 1. Numbers of BVOCs Among Growth Periods in Seven 5-year Tree Rings from *P. tabuliformis*

	Title 2	1985 to 1989	1990 to 1994	1995 to 1999	2000 to 2004	2005 to 2009	2010 to 2014	2015 to 2018
Y1	1985 to 1989	95	55	41	52	45	44	50
Y2	1990 to 1994		116	60	73	60	53	52
Y3	1995 to 1999			117	62	49	53	50
Y4	2000 to 2004				112	63	72	57
Y5	2005 to 2009					99	65	47
Y6	2010 to 2014						113	53
Y7	2015 to 2018							115



Notes: The different BVOCs were identified as: C1: Acetic acid, C2: Hydroxyacetone, C3: 1,2,3,4-Diepoxybutane, C4: 2-Nitro-1-butanol, C5: Furfural, C6: 2-Furanmethanol, C7: D-Limonene, C8: Borneol, C9: 2-(4-Methylphenyl)propan-2-ol, C10: 4,6,6-Trimethylbicyclo[3.1.1]hept-3-en-2-one, C11: 2-Octen-1-ol, 3,7-dimethyl-, isobutyrate, (Z)-, C12: Longifolene, C13: 1-Heptatriacotanol, C14: Cembrene, C15: 1H-2,8a-Methanocyclopenta[a]cyclopropa[e]cyclodecen-11-one,1a,2,5,5a,6,9,10,10a-octahydro-5,5a,6-trihydroxy-1,4-bis(hydroxymethyl)-1,7,9-trimethyl-,[1S-(1.alpha.,1a.alpha.,2.alpha.,5.beta.,5a.beta.,6.beta.,8a.alpha.,9.alpha.,10a.alpha.)], which will here on be referred to as 'Ac1mj3p2', C16: 1,7,7-Trimethyl-3-phenethylidenebicyclo[2.2.1]heptan-2-one, C17: Sandaracopimaral, C18: Methyl dehydroabietate

Fig. 1. Peak areas (%) of the 18 common BVOCs throughout the seven periods for seven 5-year period tree rings from *P. tabuliformis*

Temporal Trends of BVOCs

Of the 18 most common BVOCs, the contents of 9 increased and 9 decreased throughout the growth periods of *P. tabuliformis* (Figs. 1 and 2, and Table 2).

Increasing concentrations with increasing growth stages were found for alcohol BVOCs (*e.g.*, 2-nitro-1-butanol, 2-furanmethanol), and oxygenated monoterpenes such as 2-(4-methylphenyl)propan-2-ol and 4,6,6-trimethylbicyclo[3.1.1]hept-3-en-2-one (P < 0.05). Most alkene, acid, aldehyde, and ketone type BVOCs showed decreasing concentrations with increasing growth stages. Diterpene (*e.g.*, sandaracopimaral) and monoterpene (d-limonene) showed a significant decreasing trend (P < 0.01). Other BVOCs including acetic acid, hydroxyacetone, furfural, cembrene, 1-heptatriacotanol, and methyl dehydroabietate showed negative non-significant trends.

Terpenoid groups from BVOCs profile showed different trends in this study. Monoterpenes and diterpenes showed significant decreased trends, while sesquiterpenes and several oxygenated monoterpenes showed increased trends. With a significant decreased trend along growth stages, sandaracopimaral showed higher concentrations ranging from 7.73% (Y1) to 3.67% (Y7) and d-limonene had less concentration from 1.47% to 0.57% (Y1 *vs*. Y7). Longifolene showed an increased trend with a higher mean concentration level as 0.759%/yr along the seven growth stages. In this study oxygenated monoterpenes (such as 2-(4-methylphenyl)propan-2-ol and 4,6,6-trimethylbicyclo-[3.1.1]hept-3-en-2-one) also showed significantly increasing trends with mean concentration from 0.312% to 1.867% (Y1 *vs* Y7).

Table 2. Mann-Kendall Test Results of the 18 Common BVOCs from *P. tabuliformis* 5-Year Tree Rings Throughout the Period 1985 to 2018

Compound Name	VIA	tau	2-Sided p Value
Acetic acid	C1	-0.0476	1
Hydroxyacetone	C2	-0.0476	1
1,2,3,4-Diepoxybutane	C3	0.0476	1
2-Nitro-1-butanol	C4	0.8095	0.0163**
Furfural	C5	-0.0476	1
2-Furanmethanol	C6	0.7143	0.0355**
d-Limonene	C7	-0.6191	0.0715*
Borneol	C8	0.4286	0.2296
2-(4-Methylphenyl)propan-2-ol	C9	0.8096	0.0163**
4,6,6-Trimethylbicyclo[3.1.1]hept-3-en-2-one	C10	1	0.0027***
2-Octen-1-ol, 3,7-dimethyl-, isobutyrate, (Z)-	C11	0.2381	0.548
Longifolene	C12	0.3333	0.3675
1-Heptatriacotanol	C13	-0.0476	1
Cembrene	C14	-0.2381	0.548
Ac1mj3p2	C15	0.4286	0.2296
1,7,7-Trimethyl-3-phenethylidenebicyclo[2.2.1]heptan-2-one	C16	-0.1429	0.7639
Sandaracopimaral	C17	-0.9048	0.0069***
Methyl dehydroabietate	C18	-0.1429	0.7639
*: P < 0.1, **: P < 0.05, ***: P < 0.01; Positive and negative tau values indicate positive and negative trends, respectively			

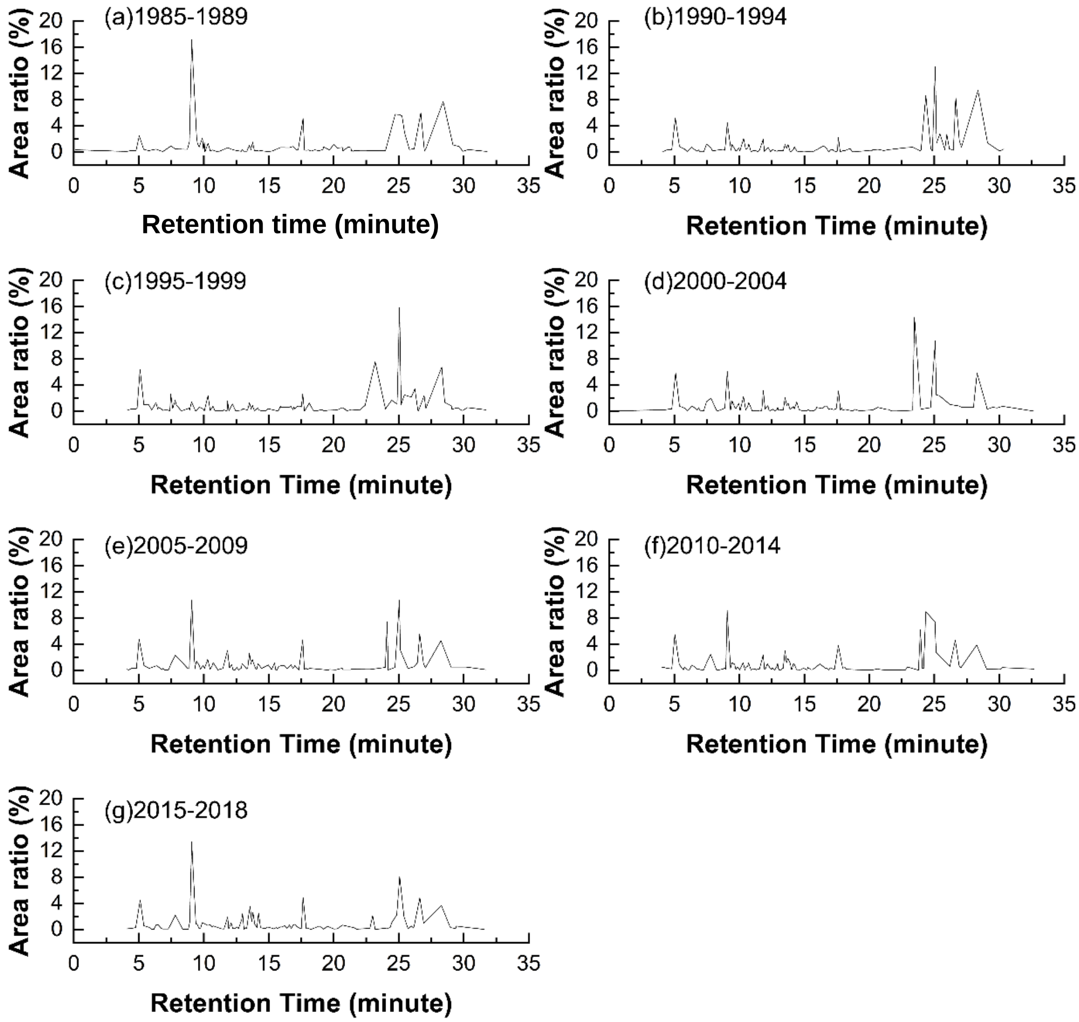
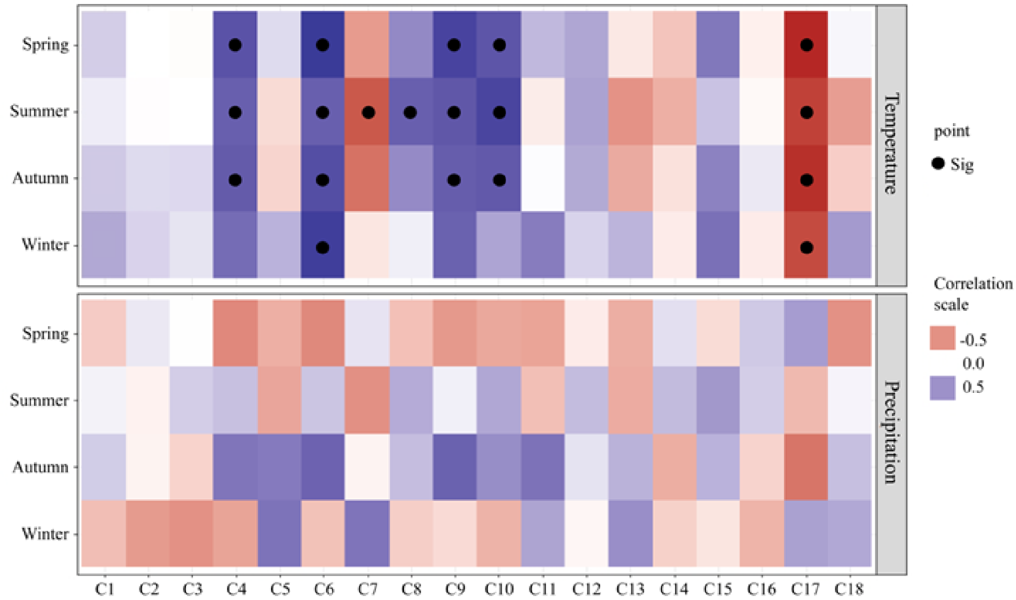


Fig. 2. Total ion chromatograms of *Pinus tabuliformis* which was extracted by ethanol and benzene/ethanol throughout the seven periods

BVOCs and Climate Parameters

With different growth stages of *P. tabuliformis*, there was a significant correlation between BVOCs concentration and seasonal temperature, but not for precipitation (Fig. 3). A significant positive correlation with warm seasonal temperature (spring, summer, and fall) was found for alcohol BVOCs (*e.g.*, 2-nitro-1-butanol, 2-furanmethanol) and several oxygenated monoterpenes (*e.g.*, 2-(4-methylphenyl)propan-2-ol and 4,6,6-trimethylbicyclo[3.1.1]hept-3-en-2-one), while significant negative correlations were found for terpenoids compounds such as d-limonene and sandara-copimaral. Except for the effect from temperature in the warm season, temperature in winter also had an important role on the storage of 2-furanmethanol and sandaracopimaral.



Notes: The different BVOCs were identified as: C1: Acetic acid, C2: Hydroxyacetone, C3: 1,2,3,4-Diepoxybutane, C4: 2-Nitro-1-butanol, C5: Furfural, C6: 2-Furanmethanol, C7: D-Limonene, C8: Borneol, C9: 2-(4-Methylphenyl)propan-2-ol, C10: 4,6,6-Trimethylbicyclo[3.1.1]hept-3-en-2-one, C11: 2-Octen-1-ol, 3,7-dimethyl-, isobutyrate, (Z)-, C12: Longifolene, C13: 1-Heptatriacotanol, C14: Cembrene, C15: Ac1mj3p2, C16: 1,7,7-Trimethyl-3-phenethylidenebicyclo[2.2.1]heptan-2-one, C17: Sandaracopimaral, C18: Methyl dehydroabietate. Significance levels were indicated as $P < 0.05$

Fig. 3. Correlation coefficients between BVOCs and seasonal mean temperature total precipitation throughout *P. tabuliformis* growth stages (1985 to 2018)

Association between BVOCs

Spearman correlation coefficients for the 18 most common BVOCs throughout the seven 5-year growth periods are shown in Fig. 4. Among terpenoids, borneol and longifolene showed significant negative correlations with acetic acid, hydroxyacetone, and 1,2,3,4-diepoxybutane, while they showed positive correlations with oxygenated monoterpenes (*e.g.*, 2-(4-methylphenyl)propan-2-ol and 4,6,6-trimethyl-bicyclo[3.1.1]-hept-3-en-2-one). In contrast, d-limonene and sandaracopimaral showed significant negative correlation ($P < 0.05$) with oxygenated monoterpenes (*e.g.*, borneol, 2-(4-methylphenyl)propan-2-ol, and 4,6,6-trimethylbicyclo[3.1.1]hept-3-en-2-one), whereas they also had significant negative correlation ($P < 0.05$) with alcohol compounds (such as 2-nitro-1-butanol and 2-furanmethanol). Except for having a significant correlation with most BOVCs, d-limonene and sandaracopimaral also showed non-significant correlation with some other BVOCs such as hydroxyacetone and 1-heptatriacotanol.

Compounds belonging to the oxygenated monoterpene groups exhibited strong positive correlations with each other, and they also showed significant positive correlations with sesquiterpenes. In contrast, monoterpenes and diterpenes were significantly positively related to each other, while they showed significant negative correlations with oxygenated monoterpenes. However, sesquiterpenes (longifolene) showed different correlations with other terpenoids. Sesquiterpenes showed significant positive correlation with oxygenated monoterpenes, negative correlation for diterpenes (*e.g.*, sandaracopimaral), and non-significant correlation with monoterpenes (such as d-limonene).

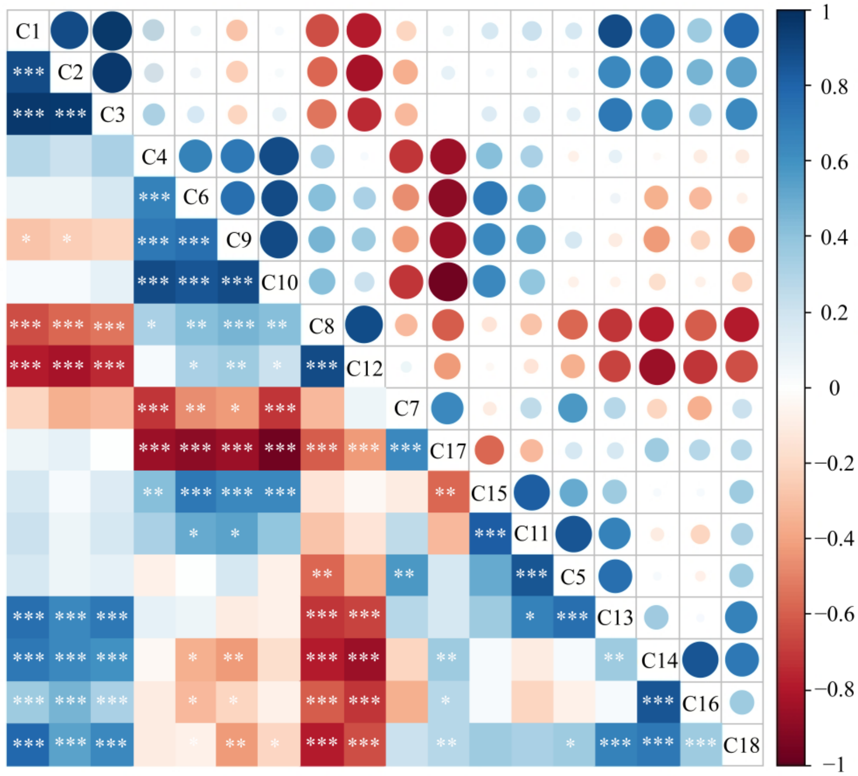


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Fig. 4. Spearman correlation matrix for BVOCs in *P. tabuliformis* across the seven 5-year growth periods throughout 1985 to 2018

DISCUSSION

Temporal Change of Chemical Components

The dendrochronological study detected 292 extractive BVOCs throughout the study period 1985 to 2018. Some of these compounds were found in every pair of different growth stages, and only 18 of the most common BVOCs were found throughout the whole multi-decadal periods. Increased concentrations along the seven growth periods were found for alcohols (such as 2-nitro-1-butanol and 2-furanmethanol) and oxygenated monoterpenes (*e.g.*, borneol, 2-(4-methylphenyl)propan-2-ol, and 4,6,6-trimethylbicyclo[3.1.1]hept-3-en-2-one). In contrast, decreased concentrations were found in monoterpenes (d-limonene) and diterpenes (sandaracopimaral) with increasing growth stages. From this study, monoterpenes concentrations decreased with high emissions and less concentration with increased growth periods in older plants. Sesquiterpenes and oxygenated monoterpenes found in the present study had more storage and less emission with increased growth stages.

A previous study reported that emission rates from mature tree branches of *Pinus pinea* were approximately twice that of young trees (Staudt *et al*. 1997). Emissions of trees increased when leaves and branches reached maturity. Similar observations have been found in studies of several coniferous species, such as *Cryptomeria japonica* and *Pinus koraiensis*, in Korea, where emitted monoterpenes were higher for older trees than younger trees (Kim *et al*. 2005). Recent studies on *P. formis* needles also suggest that BVOC volatile oils were significantly influenced by tree age in which older tree needles had more BVOC volatile oils (Duan *et al*. 2016). It was concluded that changes in chemical composition were observed at different growth stages (Bendiabdellah *et al*. 2013). Emission rates of trees were also affected by the developmental growth stage (Monson *et al*. 1995). Moreover, some studies indicated that the production/emission behavior of terpenes is correlated to synthase activities depending on plant growth stages (Holzinger *et al*. 2006). After being synthesized during photosynthesis, monoterpenes were usually stored in specialized storage structures, such as resin canals and secretory cells, and they were partly emitted by leaves to the atmosphere (Niinemets *et al*. 2004; Chen *et al*. 2019). One study in bark of *Magnolia officinalis* also showed that older trees held higher sesquiterpenes and oxygenated monoterpenes than young trees (Huang *et al*. 2023). Some compounds with increasing trend may hold more storage in special structures accompanied with less emission along with growth stages of *Pinus tabuliformis* trees. BVOCs emissions vary depending on the local biotic and abiotic factors in which the trees stand (Margarita *et al*. 2013), to some extent, BVOC concentration in *P. tabuliformis* growth rings varied depending on growth stages in this study.

Climate-Chemical Components Associations

Another important consideration that determines the rate of emission of BVOCs is temperature. The seasonal temperature had a higher effect on BVOCs of *P. tabuliformis* than precipitation in this study. A warmer environment decreased storage of monoterpenes and diterpenes but increased alcohol compounds and oxygenated monoterpenes in *P. tabuliformis.* Seasonal temperatures showed a negative correlation with BVOCs concentration of monoterpenes and diterpenes, where significant correlations were found for d-limonene in summer and sandaracopimaral in all seasons. Similar correlations were found in studies of diurnal and seasonal monoterpene and isoprene emissions that increased with increasing temperature (Chen *et al*. 2019, 2020). Monoterpene emissions were suggested as a combination of stored and immediately synthesized compounds (Staudt *et al*. 1997), in which emission peaked in warm summer (Peng *et al*. 2011; Bai *et al*. 2017; Huang *et al*. 2023) along with low storage in a specific organ. Another study showed that emissions of diterpenes were detected in different seasons (Chen *et al*. 2019), the seasonal variations of temperature-related emission may be attributed to ecological functions throughout plant development.

It was also found that seasonal temperature exerted a positive effect on BVOCs accumulation of alcohol compounds and oxygenated monoterpenes in *P. tabuliformis* in this study. Most terpenoids emissions were due to biosynthesis and temperature-dependent release from leaf storage structures (Ge *et al*. 2020; Sanchez-Martinez *et al*. 2023). Some terpenes, however, increased in plants in warmer environments, which was due to improved plant growth and larger storage space for stored terpenes such as sesquiterpenes and oxygenated monoterpenes (Sanchez-Martinez *et al*. 2023). The differences in emission responses of monoterpenes, sesquiterpenes, and diterpenes to temperature in the present study is likely related to their different temporal storage properties in needle surface waxes, and their temperature-dependent adherence and release (Joensuu *et al*. 2016). The correlation between relative content of BVOCs and temperature in the present study indicates that climatic variability could affect some temperature-dependent ecosystem processes, such as emission and storage of BVOCs and nutrient availability in forests. Temperature also affects the evaporation and emission of BVOCs from leaves to the atmosphere, and the emission of BVOCs from plants substantially affects regional climate change and global carbon budgets (Xu *et al.* 2015; Peng *et al*. 2020). When temperature is above the threshold of the enzymes responsible for the synthesis, enzyme denaturation might cause BVOCs releasing and spreading along a vapor pressure gradient in cellular compartments from high concentrations outward (Margarita *et al*. 2013). With climate warming, the more volatile compounds may be more likely to become evaporated and lost from the wood into the air, whereas the more oxygenated compounds would be less volatile, and that could explain their greater presence in the wood material after the passage of time. However, this study was only conducted in compound variation of individual species. Further studies on long-term emission and storage of BVOCs of different species are needed to better investigate and understand the correlation between BVOCs variation and climatic change.

Association between BVOCs

In this study, the BVOCs in *P. tabuliformis* showed complex and different correlations with one another. Monoterpenes and diterpenes had significant negative correlations with oxygenated monoterpenes, and sesquiterpenes (longifolene) showed different correlation with monoterpenes (such as d-limonene), oxygenated monoterpenes and diterpenes (*e.g.*, andaracopimaral). Strong positive correlations between oxygenated monoterpenes across age/periods suggested their formation might occur *via* the same pathway (Chen *et al*. 2020). In the present study, longifolene significantly correlated with borneol and showed similar correlation with other chemical components. It has been shown that monoterpene, sesquiterpene, and oxygenated monoterpene originate from different biosynthesis pathways and their synthesis and emission may largely influence storage in tree stem (Pazouki and Niinemets 2016; Wang *et al*. 2023).

Limonene was one of the dominant monoterpenes in *P. tabuliformis* and increased with growth periods in this study. Limonene showed a strong negative correlation with oxygenated monoterpene storage while with a non-significant correlation with sesquiterpene accumulation. This finding is similar to a recent study showing that the emission of monoterpenes and sesquiterpenes were very different from oxygenated monoterpenes, and the differences might originate from diverse biosynthetic pathways, emission controls, and storage patterns (Kim *et al*. 2005; Chen *et al*. 2020). Sandaracopimaral had a significant positive correlation with longifolene and showed a similar correlation with monoterpenes, oxygenated monoterpenes, sesquiterpene, among other compounds. Temporal changes and temperature associations of sandaracopimaral were similar to limonene in this study, suggesting a strong influence from mean annual temperature in this study zone.

CONCLUSIONS

1. The biogenic volatile organic compounds (BVOCs) concentrations in *P. tabuliformis* tree were different among the different growth stages with only 18 of the same BVOCs throughout the full growth periods.
2. Increasing trends were found for alcohols and oxygenated monoterpenes, whereas decreasing trends were found for monoterpenes and diterpenes.
3. The contrasting trends of stored BVOC contents decreasing and increasing with growth stages might be due to their responses to the changes in environmental factors.
4. The present study showed that dendrochronology is a suitable method for re-establishing the biological effects from historical climate variability on tree key species, which is important to discuss forest ecosystem services and predict future environmental effects of global warming.

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