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Factors Affecting Ambient Monoterpene Levels in a Pine Forest

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The concentration levels of monoterpenes, including α- and β-pinene, were measured in a pine forest in Florida, USA, over about one year. Based on this measurement data, the current study then investigated the factors affecting the environmental behavior of monoterpenes. Despite a moderately weak temperature variability in the study area, the temperature dependence of the concentration variations was still evident. The concentrations of the two pinenes were significantly affected by changes in the air temperature, as indicated by strong correlations with temperature. A close relation among the measured parameters was also found between the β-pinene and ozone concentrations, which is also in line with previous findings from other studies. In addition, it was interesting to note that the β/α pinene concentration ratio exhibited a strong inverse correlation to temperature, with the seasonal mean ranging from 0.51(summer) to 0.93(winter). Accordingly, the current results indicate that, in a forest environment, the major terpene species concentrations are affected by both meteorological conditions and chemical reactions.

Key words : VOC, factor, volatile, ozone, monoterpene

1. Introduction

In recent years, there has been a growing interest in the potential environmental effects of global climate changes. Of specific interest is the role that climate changes may play in altering natural volatile organic compound(NVOC) emissions from trees and perturbing air quality(e.g., ozone formation). The measurements of NVOC emissions in the 1960s suggested that global and continental scale emissions from natural sources overshadowed those from anthropogenic sources[1,2]. In addition, the potential effect of NVOC emissions on ozone formation has attracted a great deal of attention due to the possible influence of ozone on the production of acid deposition species. Since the atmospheric chemistry of sulfur dioxide, nitrogen oxides, and reactive VOCs is coupled in a complex way, natural hydrocarbon emissions have become an important input requirement for both regional acid deposition and photochemical oxidant models[3].

Therefore, in an attempt to offer some insights into the factors and processes regulating the ambient monoterpene levels, the concentrations of monoterpenes, including the two major species of α- and β-pinene, were measured in a pine forest in Florida, USA, during 1994 and 1995. The relationships between their concentration levels and concurrently measured environmental parameters were then investigated in an effort to explain the factors and processes regulating the environmental behavior of NVOCs in a forest environment.

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2. Experiments

2.1 Sampling Site

The study site was located in the Austin Cary Forest in a two-hectare cleared area surrounded by commercial pine plantations(see Figure 1), approximately 15 km NE of the downtown business district of Gainesville in the north central region

of Florida, USA. Routine monitoring of the air quality, meteorology, and acid deposition, along with open-top chamber studies had been conducted at the site since 1988. The local sources of air pollution within a 10 km radius of the monitoring site were as follows. A heavily traveled highway (State Route 24) was the closest, approximately 0.4 km NW. Small paved roads with light traffic loads were also located within a 5 km radius. Moreover, the principal stationary sources within a 20 km radius of the site included Gainesville Regional Utilities and the Deerhaven coal burning and Skelly oil burning power plants. The major regional industrial source was the Georgia Pacific paper pulp mill at Palatka approximately 60 km east. The ambient air samples were collected 20 m apart from the air quality monitoring shelter at a height of 1 m above ground.

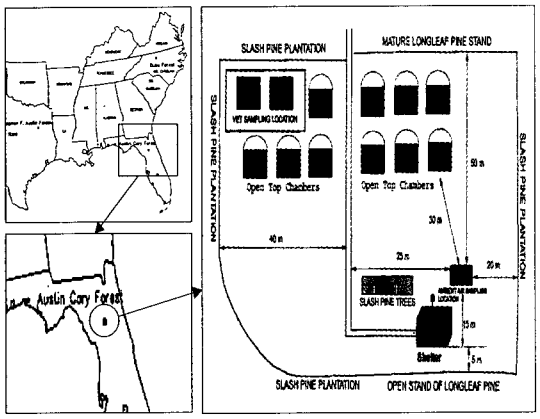

Fig. 1. Site map of study location in Austin Cary forest in north central region of Florida.

2.2 Sampling and Analysis

The NVOC samples were collected using the Tenax-TA sorbent once or twice a day at intervals of several days(or weekly). Most of the sampling was conducted during the daytime(typically between noon and 6 PM) over a total duration of one to two hours. The VOC analysis was conducted using two GC systems interfaced with an automated cryogenic focusing system(Tekmar, Model 5010-GT Automatic Desorber). The protocols used for the sampling and analyses were specifically developed for taking monoterpene measurements.

For the NVOC collection, the sampling tubes were pyrex glass tubes(OD 1.27 cm ; length 18.1 cm) filled with 900 mg of Tenax-TA. The samples were collected in these Tenax-filled tubes via a rechargeable personal air sampler(Model PAS-3000, Supelco) and sampling adaptor(#14-1486-200, Tekmar), consisting of a sampling tube holder, O-rings for the sampling tube, and metal filter made of nickel[4]. The samples were stored in a clean tube container(Tekmar) until used for an accuracy(or recovery) test. Some of the Tenax sampling tubes were spiked in the laboratory with a mixture of VOCs(i.e., several terpene species (α-pinene, β-pinene, d-limonene, p-xylene, and methanol) and transported to the field site. The Tenax sample tubes were exposed to ambient air for a few minutes at the field site and then transported back to the laboratory. For the analysis of the natural VOCs, two individual GC systems, GC-ITD and GC-FID, were selected from the same manufacturer with similar model numbers(Perkin Elmer, GC-8420 and -8500). The systems were equipped with the same DB-5 capillary column and operated under the same analytical conditions. The recoveries of all the terpene hydrocarbons were found to be within a 95 to 105 % range after one to 5 days of storage at room temperature. In addition, during the ambient air-sampling excursions, a known amount of p-xylene was also occasionally spiked using a clean sampling tube. The mean and relative standard deviation for the recovery rate of the spiked p-xylene samples was 98.1 and 3.2 %, respectively(N=6). The breakthrough volumes were also tested using different quantities of terpenes at different sampling flow rates. The experimental results, derived using two sorbent tubes in series, revealed about a 50 % breakthrough with a loading of 150 ng of α-pinene at a flow rate of 0.86 l min^{-1}(at 38 ℃). When the precision of the NVOC measurement technique was tested in a triplicate analysis of field traps loaded with known quantities of the two pinenes, the result was less than 10 %. The detection limit for monoterpenoid species was found to be ~ 2pptv.

3. Results and Discussion

3.1 Factors affecting natural VOC levels in the study site

The concentrations of α- and β-pinene deter-

mined during the study period averaged at 125±86 (N=65) and 86±52 pptv(N=56), respectively. To examine the effects of surrounding conditions on the environmental behavior of natural VOCs, a correlation analysis was conducted between the VOC concentrations and relevant parameters investigated concurrently. The results, as shown in Table 1, revealed that the two pinenes were significantly correlated to each other, indicating similar source processes for both species. The influence of temperature on the observed concentrations was also evident. It is already known that temperature is a driving force for VOC emission processes in a forest environment[5]. Hence, monoterpene species are generally expected to exhibit positive correlations with air temperature, unless they are subordinate to significant chemical removal and/or physical dilution processes. For example, studies by Yokouchi and Ambe[6] reported a significant correlation between monoterpenes and temperature. The results of the current correlation analysis also indicated that the concentrations of both pinenes were strongly correlated with the air temperature. Moreover, the magnitude of the correlation strengths fell within a comparable range: α-pinene(r=0.5240) and β-pinene(r=0.5050). It was also interesting to find out that the β/α ratio exhibited a strong inverse correlation with temperature, whereas the individual species exhibited a positive correlation(Figure 2). The inverse relation was quite evident in that the seasonal mean values were clearly distinguished between the lowest β/α value of 0.51(at the peak of summer) and highest value of 0.93(in the dead of winter). If the observed pattern fairly reflects the relationships, the temperature-dependence of the two pinenes appears to be highly systematic. This type of relationship is often expressed numerically by combining the temperature-normalized emission rate and empirical coefficient[7], as such, the β/α relationship from the current study would seem to essentially fit the generalized formula for temperature dependence.

It is reasonable to expect that the local ozone concentrations will exert a direct influence on the ambient terpene levels. Inspection of the overall measurement data from the present study also indicated such a possibility. Whereas the β-pinene concentrations exhibited a strong inverse correlation with ozone, such a relationship appeared to be less significant for the α-pinene concentrations(Figure 3). It is interesting to note that β-pinene has a greater potential for ozone production than α-pinene[8]. However, despite the existence of a strong inverse correlation between the pinenes and ozone, the changes in the terpene levels may not simply be the direct consequence of destruction due to ozone(and/or other oxidants like OH). It has also been suggested that meteorological con

Table 1. Results of correlation analysis between natural VOC species and relevant environmental parameters

	α-pinene	β-pinene	β/α	Temp (℃)	RH(%)
α-pinene	1.0000				
β-pinene	0.8889	1.0000			
β/α	-0.5425	-0.2079	1.0000		
Temp (℃)	0.5240	0.5050	-0.6119	1.0000	
RH(%)	0.1239	0.3325	0.1260	-0.0082	1.0000

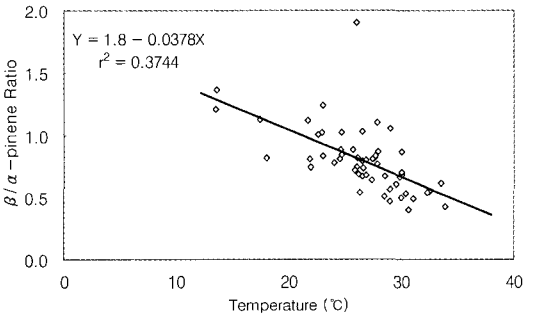

Fig. 2. Plot of relationship between β/α pinene ratio and temperature in Austin-Cary forest.

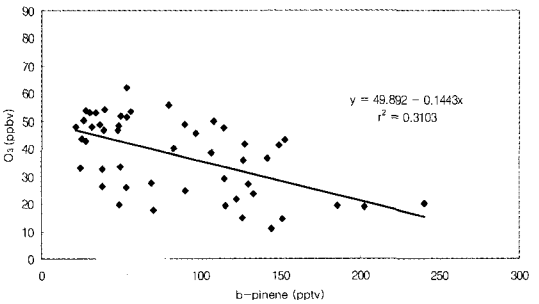

Fig. 3. Plot of relationship between β pinene and ozone levels in Austin-Cary forest.

ditions may be more influential in determining the concentration levels of ozone or terpenes in a forest environment than chemical reactions[5].

3.2 Temperature as one of the major factors for controlling NVOC levels

It has already been demonstrated that the emission rates of NVOCs from conifers exhibit a strong correlation with environmental parameters, like temperature[9]. The emission rates of terpenes can also be expressed by the following equation:

$$\ln(ER) = a + b(T), \quad (1)$$

where ln(ER) is the natural log of the terpene emission rate (ng terpene (g dw)$^{-1}$ h^{-1}), T is the environmental temperature (℃), and a and b are the constants determined empirically[9]. Based on the fact that slash pines were the major source of monoterpenes at the current study site, the ambient concentrations of the major monoterpenes were expressed using the following equation and certain assumptions, including weak chemical reactions and homogeneous mixing of the ambient air.

$$\ln(AC) = c + d(T), \quad (2)$$

where AC is the ambient concentration of monoterpenes (pptv), c and d are the constants determined empirically.

These two equations were applied to the two data groups divided seasonally. Representative plots for summer and winter are shown in Figures 4a and 4b, respectively. For a better description of the terpene behavior, the temperature-dependence was checked with both concentrations,

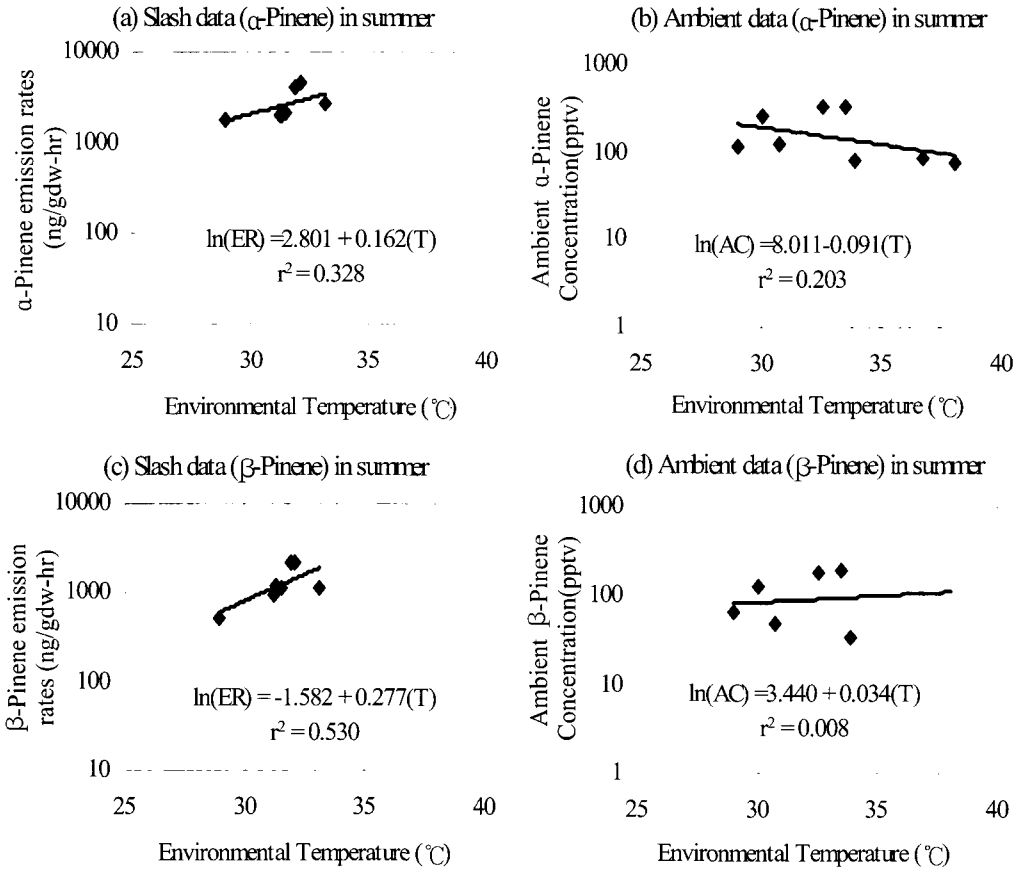

Fig. 4a. Relationship between temperature and terpene levels in ambient air and slash pine emissions during summer.

along with the emission rates, as determined by Kim[10]. In general, the emission data from the slash pines was suitably applied to Tingey's equation. In particular, the α- and β-pinene emissions in the fall season exhibited a relatively strong correlation with the environmental temperature (r^2 > 0.6). It was also found that the β-pinene emissions generally exhibited a slightly stronger relationship with the temperature than the α-pinene emissions. Conversely, the ambient monoterpenes did not reveal as strong a relationship with the temperature as the slash emission data for both pinenes. Except for in winter, the ambient concentration levels of α-pinene maintained a slightly stronger relationship with the temperature than the β-pinene levels, in contrast to the emission data.

The concentrations observed during the summer varied inversely with the temperature(see Figure 4a). The active chemical reactions occurring under the strong sunlight during this season may have produced the poor correlation. However, Harrison[11] reported that the main sinks of monoterpenes, i.e. OH radicals and ozone, are significantly reduced at night. Hence, the ambient monoterpene levels can be relatively high at night, as seen from other studies[6,8,12~16]. It was also observed that the winter α- and β-pinene concentrations exhibited the strongest correlation with temperature(see Figure 4b). Since it can be assumed that the solar radiation and temperature are lowest in winter along with comparatively low relative humidity(RH) values, the concentration of OH radicals may have been moderately reduced, thereby affecting the β-pinene levels. In fact, the relationship between the β-pinene concentration and temperature measured in the winter exhibited a relatively strong correlation(r^2 = 0.352), while

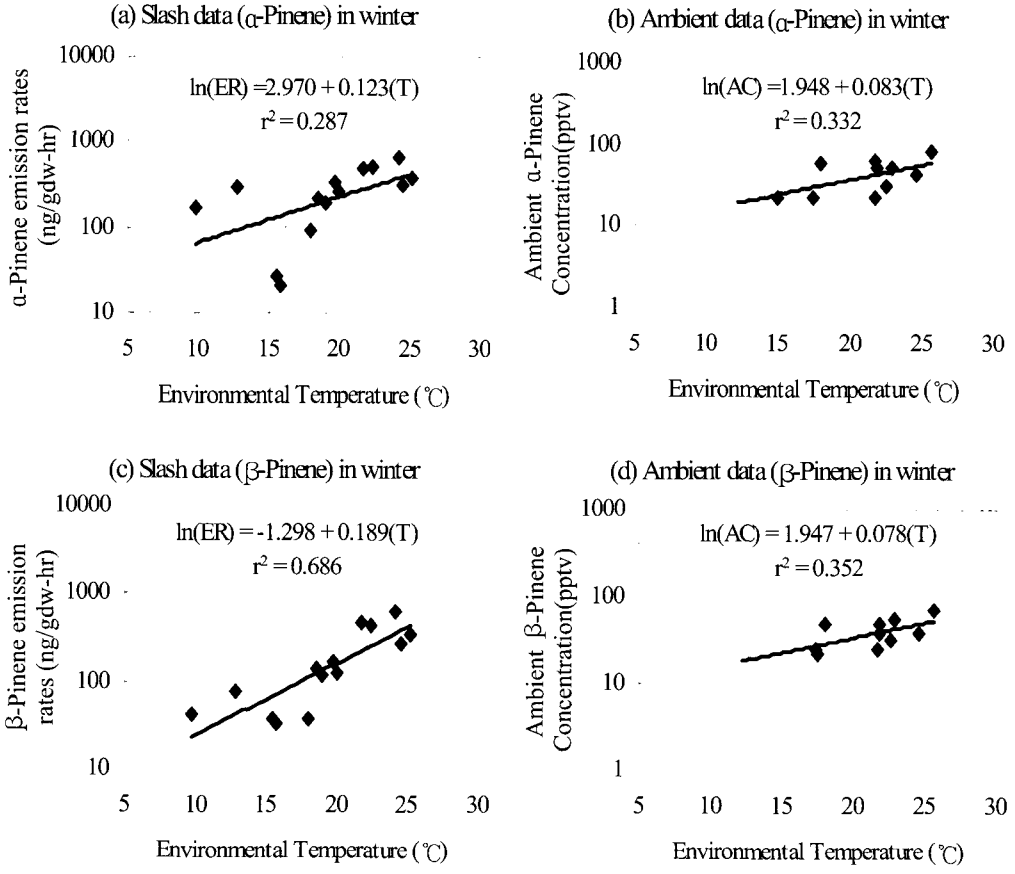

Fig. 4b. Relationship between temperature and terpene levels in ambient air and slash pine emissions during winter.

no such relationship existed during the other seasons(r^2 < 0.066).

3.3 Emission sources and sinks of terpenes

The β/α pinene ratios were compared with slash emission rates and ambient concentrations across the seasons(Table 2). It was found that α- and β-pinene were the major(about > 90%) monoterpene compounds in the slash emissions and ambient natural VOCs levels. It was also found that the β/α emission ratios varied less during the spring and summer than during the other two seasons. The emission ratios were most irregular during the fall, indicating considerable variations in the fractional distributions of monoterpenes during this season.

Table 2. Seasonal comparison between slash emission and ambient concentration β/α ratios

Season		Slash pine	n	Ambient air	n
Spring	β/α	0.36±0.07	7	0.71±0.18	7
	Range	0.28~0.47		0.42~0.87	
Summer	β/α	0.48±0.09	7	0.51±0.09	6
	Range	0.29~0.57		0.40~0.62	
Fall	β/α	0.72±0.54	7	0.63±0.11	7
	Range	0.29~1.73		0.47~0.80	
Winter	β/α	0.85±0.16	5	0.96±0.15	5
	Range	0.59~0.97		0.75~1.13	

During the winter season, when the solar radiation intensity and ambient temperature were lowest, the slash emission and ambient concentration data were very tightly related, as seen in Table 2. Hence, this observation suggests that the slash pines were the main source of terpenes present in the forest air, as they represented about 90 % of all the trees in the Austin Cary Forest. Consequently, it was assumed that the chemical reactions in the atmosphere were very slow during the winter, plus the air was well mixed due to inversion break-ups in the afternoon under windy conditions. Conversely, in the current study, the ambient concentration β/α ratios remained less variable than those determined by the slash pine emissions. The discrepancies between the slash emission and ambient concentration β/α ratios were largest during the spring season. The ambient air ratio values were found to be approximately two times higher than the slash pine values. This significant discrepancy may have been because the daytime α-pinene reaction rate was faster than the β-pinene rate during the spring. Atkinson[8] previously summarized the chemical reactivity between several monoterpenes and ozone and between monoterpenes and OH radicals, and stated that the relative reactivity of α-pinene with ozone is 5.3 times higher than that of β-pinene. He also reported that the relative reactivity of β-pinene with OH radicals is 1.2 times higher than that of α-pinene.

The relative enhancement of the β/α ratios in the ambient monoterpene concentrations in the fall and winter can be partly explained by the higher slash pine emissions during those periods, as seen in Table 2. The slight differences between the ambient concentration and emission rate β/α ratios in the last two seasons can also be explained by the relatively low solar radiation and temperature.

4. Summary

The current study investigated the factors affecting monoterpene concentrations in a pine forest based on data sets acquired over about one year. As a result, α- and β-pinene were identified as the major(about > 90%) monoterpene compounds in the slash pine forest in terms of both the emission strength and the ambient concentration level. Based on the emission data, the β/α ratios varied less during the spring and summer than during the other seasons. During the winter season with a low solar radiation intensity and temperature, the slash emissions and ambient concentration levels of terpenes were found to be very tightly related.

In general, the emission data from the slash pines was suitably subject to Tingey's equation, wherein emission is highly temperature-dependent. In fact, it was found that the emissions of α- and β-pinene in the fall season exhibited a strong correlation with the environmental temperature. Conversely, the ambient concentrations of monoterpenes did not exhibit such a strong relationship with temperature. Similarly, diverse types of relationships

between the terpene data sets and temperature were observed across the seasons. The overall results of the current study indicated that α - and β -pinene were significantly correlated with each other, suggesting similar source processes for both species. It was also found that the β / α ratio exhibited a strong inverse correlation with temperature. However, the current results also indicate that, in a forest environment, the major terpene species concentrations were not only affected by meteorological conditions but also by chemical reactions. Since there are likely many other factors involved in the distribution of NVOCs in ambient air, extended studies are needed at different locations and under different environmental conditions to produce a reliable NVOC database.

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