Chinese Chemical Letters Vol. 13, No. 9, pp 897 – 900, 2002
http://www.imm.ac.cn/journal/ccl/html

Biogenic Isoprene Emission Mechanism from $^{13}CO_2$ Exposure Experiments

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Abstract: Biogenic isoprene emissions have been believed to be from only photosynthesis processes in plant. However nocturnal isoprene emission from pine is detected. And by feeding $^{13}CO_2$ to plants, it is found that both photosynthesis pathway and light independent processes contribute to isoprene emissions.

Keywords: Emissions, volatile organic compounds (VOCs), ^{13}C labeling, isoprene.

Isoprene is one of the volatile organic compounds (VOCs) which has received the most attention because of its significant amount of emission from vegetation to atmosphere[1]. Photosynthetically active radiation (PAR) is found to be essential for isoprene emission[2-4].. Based on these understanding, an algorithm was developed to quantify isoprene emission rates[5]. Experimental results of nocturnal isoprene emissions and $^{13}CO_2$ exposure to pine plants show that above understanding of isoprene emission mechanism is imcomplete. This paper reveals a plausible light independent emission process from plants which may be helpful for a better estimation of isoprene emissions.

Experimental

The experiments are performed in reactor with pine plants (*pinus sylverstris*) growing inside. The reactor is a 1600 L volume glass chamber with devices equipped for monitoring temperature, light intensity. The concentrations of CO_2, H_2O and VOCs at chamber inlet and outlet are measured simultaneously. The light intensity is 360 μE $m^{-2}s^{-1}$ under full illumination at mid canopy of pines in the chamber, and varies at minimum step of 30 μE $m^{-2}s^{-1}$.

The emission rate of VOC species emitted from pine is calculated by:

$$\Phi_{VOC} = \frac{F}{A_L}([VOC]_{out} - [VOC]_{in}) + \Phi_{wall} \quad (1)$$

where Φ_{VOC} is emission rate of certain VOC species (mol cm^{-2} s^{-1}); F is flow rate of air through the chamber; A_L is leaf areas of pine (one side); and $[VOC]_{out}$, $[VOC]_{in}$

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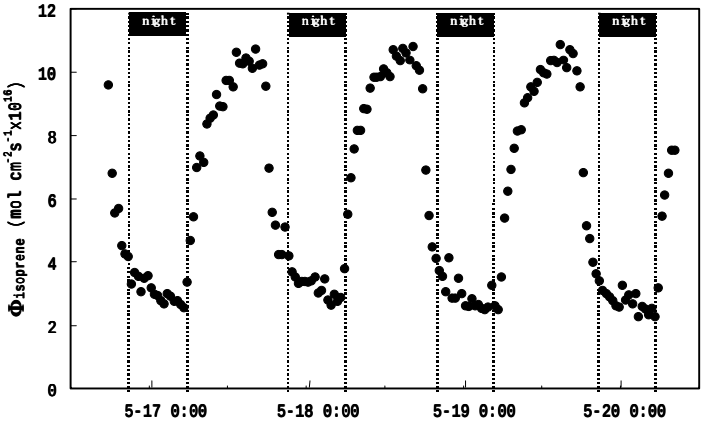
is mixing ratio of VOC species at chamber inlet and outlet respectively. Wall losses, Φ_{wall} is tested and is negligible for isoprene.

Pure $^{13}CO_2$ gas is diluted by CO_2 free synthetic air to ambient concentration (about 350 ppm by volume), and then used to feed pine plants. The $^{13}CO_2$ is fed for eight hours, and then it is switched back to normal CO_2. During the whole period of $^{13}CO_2$ fumigation, light intensity was set at 300 μE $m^{-2}s^{-1}$ and leaf temperature is 20°C.

Results and Discussion

Isoprene emission rates are calculated by equation (1). Isoprene emissions show distinct diurnal variation (**Figure 1**). Over a time period of 4 days, the uncertainties of emissions at constant temperature and light intensity are within 15%. It is evident that emissions at night are not negligible. Under the condition of our measurement, daytime emission is about 4 times as that in darkness for both compounds, this difference is caused by the variation in temperature as well as light intensity.

Figure 1 Diurnal variation of isoprene emission rates (day: 22.5°C, 360 μE$m^{-2}s^{-1}$; night: 15°C)



Measurements show that isoprene emission rates change with season. The emission rates shown in **Figure 2** are the results normalized to 360 μE$m^{-2}s^{-1}$ light intensity and 25°C leaf temperature. The highest emission rates of isoprene are obtained in mid of May, and drop from early July quite rapidly. In **Figure 2** the nighttime emission rates of isoprene are also plotted. Leaf temperatures are normalized to 25°C as well. Nocturnal isoprene emission rates are about 1/3 of that at daytime.

The mass spectra of isoprene from pine are measured on GC-MS system before, during, and after $^{13}CO_2$ feeding to plants (**Figure 3**). During $^{13}CO_2$ fumigation, the relative abundance of ion at *m/z*= 67 drops significantly. Meanwhile the ion 73, hinting the full labeling of isoprene molecule, has the simultaneous increase with ion 45, and drops immediately while $^{13}CO_2$ is removed. The ion 69, suggesting the lower number of carbon atoms labeling, has long term elevated level even after the removal of $^{13}CO_2$ ..

Figure 2 Seasonal variation of daytime and nighttime isoprene emissions rates

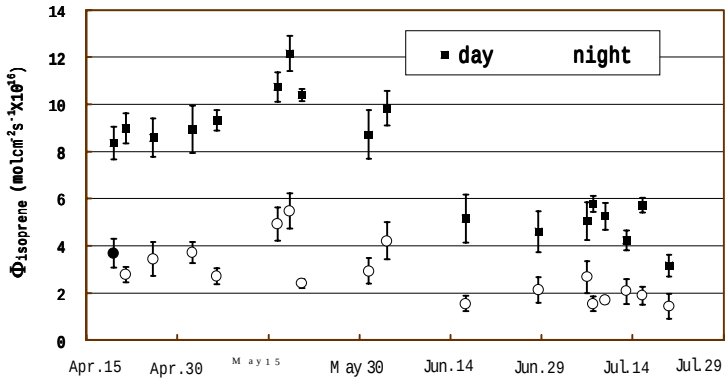
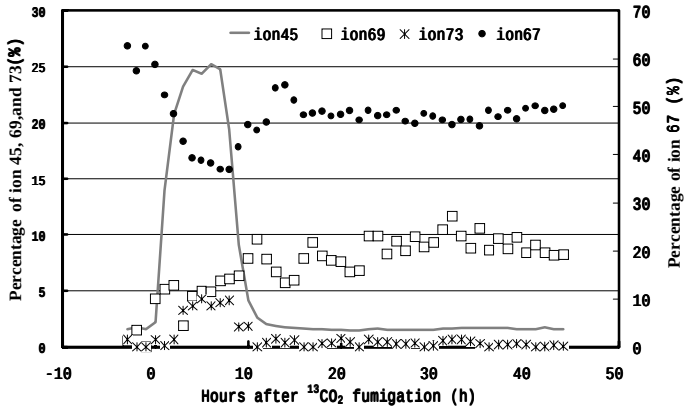


Figure 3 The variation of isoprene mass ions during and after $^{13}CO_2$ exposure

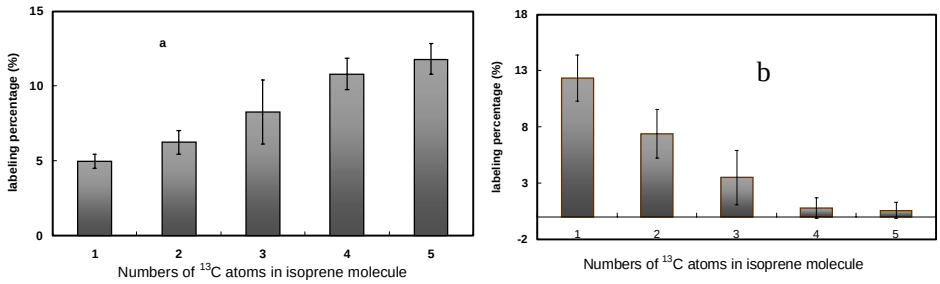


The aggregated percentage of isoprene incorporated by ^{13}C reflects the contribution of photosynthesis to isoprene emission. The variation of percentages during $^{13}CO_2$ exposure is shown in **Figure 4a**. The isoprene labeling lasts for another 48 hours after $^{13}CO_2$ supply is stopped (**Figure 4b)**. Our measurements show a fast but incomplete labeling of isoprene by ^{13}C. However during the whole 8 hours of $^{13}CO_2$ fumigation, the aggregated labeling possibility of all patterns is not higher than 45%, which means that up to 45% isoprene molecule are ^{13}C labeled and therefore this part is directly related to photosynthesis.

The interesting result is that isoprene is still labeled even several tens of hours after $^{13}CO_2$ is replaced by normal air. It is more important to note from **Figure 4b** that the isoprene labeling has different features when $^{13}CO_2$ is supplied and after it is washed out. During the $^{13}CO_2$ exposure period, isoprene is preferentially to be fully labeled, but when normal CO_2 is used afterwards, isoprene is favored to have only one or two ^{13}C atoms incorporated into the molecule，and the latter process lasts for long time during which

pine plants are in darkness for 8 hours , but no differences are found for the labeling of labeling behavior between daytime and night time.

Figure 4 The labeling of isoprene molecule during and after $^{13}CO_2$ exposure



Conclusion

Lichtenthaler *et al*. reported an alternative biosynthesis pathway of isoprene intermediate, GAP/pyruvate[6].. Because PAR is not necessary for the alternative pathway, it may work in darkness. And due to the large buffer for carbon source in the new pathway[6], the isoprene produced in this process needs longer turnover time from CO_2 assimilation, and also less carbon atoms fixed by photosynthesis are used. Therefore, the labeling is slower and more favor to lower numbers of carbon atoms incorporated by ^{13}C.

References

1. T.D. Sharkey. *Endeavour*, **1996**, *20*,74.
2. S.P.J.Shah, L.J.Rogers, *Biochem., J.*, **1969**,*114*, 395.
3. T. D. Sharkey, E.A.Holland, H.A.Mooney, *Trace Gas Emission by Plants*, Academic press, **1991**,153.
4. J.-P.Schnitzler, A.R.Steinbrecher, A.Lehning, *Liebl. Bot. Acta.*, **1996**,*109*,216.
5. A.B.Guenther, P.R.Zimmerman, P.C.Harley, R.K.Monson, R.Fall, *Journal of Geophysical Research*, **1993**, *98* (D7), 12609.
6. H.K.Lichtenthaler, M.Rohmer, J. Schwender, *Physiologia Plantarum*, **1997**,*101*, 643.

Received 19 December, 2001