

SCREENING THE SUBTROPICAL TREES FOR LOW ISOPRENE EMISSION IN TAIWAN

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ABSTRACT

Since isoprene may react actively with nitrogen oxides to produce ozone in urban atmosphere, the urban trees with high isoprene emission rate have recently obtained great concerns in Taiwan. It is on this purpose that Taiwan EPA initiated a project to screen the subtropical or tropical trees with low or no isoprene emission rate. A PP plastic bag enclosure method in combination with a GC-FID instrument installed with a Se-30 packing column was adopted in this study to quickly detect the tree gas emission. Totally 28 popular tree species were screened in the first stage in 2003. Among them seven species were found to be isoprene emitters. They are mango, Formosan sweet gum (*Liquidambar formosana*), sissoo tree (*Dalbergia sissoo*), white bark fig (*Ficus benjamina*), rubber plant (*Ficus elastica*), poongaoil (*Pongamia pinnata*), and Ceylon olive (*Elaeocarpus serratus*), with emission rate of 39.5, 38.4, 41.4, 27.7, 21.1, 12.4, and 14.8 $\mu\text{g g}^{-1} \text{h}^{-1}$, respectively. The results suggest that these species should be avoided or limited in urban reforestation, although there is no direct evidence showing that the emitted isoprene is the principal precursor responsible for the raised ozone level in four urban areas in Taiwan.

Key words: Isoprene; Ozone; Reforestation; Urban air quality; Taiwan

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INTRODUCTION

Since isoprene (C_5H_8) may react actively with nitrogen oxides to produce ozone in urban atmosphere [2,4,6, 31], the urban trees with high isoprene emission rate have recently obtained great concerns in Taiwan. Isoprene is a highly reactive, naturally produced hydrocarbon. It is the major component of natural rubber. Since isoprene could be emitted from a lot of tree species, include oak, maple, *Ficus* spp [1, 9, 10,11, 18, 22, 25-29], this gas is thought to be the most important component of biogenic volatile organic compounds. Recent estimates suggest that isoprene is the most abundant hydrocarbon across much of the eastern U.S. [8, 12, 13,15, 19,20] and other continent [5, 11,14, 21,23, 24, 32].

Analyses of isoprene reactivity, in the context of ozone formation, suggests that isoprene is the dominant hydrocarbon in the rural atmosphere and an important hydrocarbon in the urban atmosphere [2, 16, 30, 31].

It is on this purpose that Taiwan EPA initiated a project to screen the subtropical or tropical trees in Taiwan for their isoprene emission rate. Another goal of this is to measure the uptake rate of ozone by tree plants so that people can choose the highest pollutant-absorbing plants as well as the lowest isoprene-emitting plants for growing in the urban and rural areas around the islands.

MATERIALS AND METHODS

Instrument and Measurement of Isoprene

A HP6890 gas chromatograph previously used in measuring ethylene by flame ionization detector (FID) in Taipei [3] and the concept for detecting peroxyacetyl nitrate at Taipei [30] was adopted in this isoprene study. The separation column of Se-30 reported by Keller & Lerdau [16] was adopted. It is a 1.68-m-long x 3.2-mm-diameter packed column with 5%Se-30 on a 100/120 mesh Chromosorb G support. Each time an air sample of 1 mL was manually introduced into the instrument using a gas-tight syringe. The carrier gas was ultra-pure nitrogen at flow rate of 8.6 mL/min. The Se-30 column was maintained at 60 C for gas separation. The detector temperature was 250 C, while the injector temperature was 120 C.

Under these conditions the retention times for ethylene and isoprene were 0.61 min and 0.92 min, respectively. The column was cleaned thermally by elevation of the temperature to 150 C overnight whenever needed.

The standard isoprene gas was prepared following the procedure reported by Sharkey [25, 27,29]. Each time a 20 ul of pure frozen liquid isoprene (Sigma Co.) was evaporated in a 2-liter glass bottle with Teflon stopper, then a 0.8 mL of the bottle air was diluted into another 2-liter glass bottle to make a standard isoprene gas of 2.0 ppm for calibration.

Screening of Common Tree Species for Isoprene Emission in Taiwan

For measuring the isoprene emission rate of a tree, the PE bag enclosure method as reported by Lerdaun & Keller [21], Fukui & Doskey[7], and Kempf et al.[17] was adopted and modified for use in this study. Instead of PE bag, a 5-liter transparent PP bag was used to enclose a branch for 5-10 minutes. After gentle shaking, a 5-mL gas-tight syringe was used to take the air sample inside the bag, and 1 mL of the air sample was injected into the GC. The real enclosure volume was estimated by measuring the in situ dimensions of the PP bag. A preliminary test showed that under normal sun light the temperature will be raised to 3-5 degrees C higher than the ambient, and the isoprene concentration also accumulate to the highest in 5-10 min for most plants. Preliminary test also showed that at downwind areas of a branch or a tree, there is no detectable isoprene, therefore the emission rates was estimated by the following equation:

$$E \text{ (ug/g/hr)} = [C_t - C_0] \times V/t \times 1/W_{dm}$$

Where E is the emission rate, C_t is the isoprene concentration in enclosure bag after t mins, C_0 is the background isoprene concentration and is 0 in this study, V is

the estimated enclosure volume in liter, t is the real enclosure time, and W_{dm} is the dry weight of the enclosed leaves.

Comparison between Ambient Concentrations of Ethylene, propylene and Isoprene

As ethylene was a dominant pollutant gas at Taipei, we tried to compare the ambient concentrations of both ethylene and isoprene. The measurement of ethylene also uses the same Se-30 column and use the same GC conditions. Under the same conditions the retention times for ethylene, propylene and isoprene were 0.61, 0.68 and 0.92 min, respectively.

Each time a 5-mL air sample was taken from the ambient air at National Taiwan University Farm. A 1-mL portion was injected into the GC and the concentrations of ethylene, propylene and isoprene was determined by compared with standard gas of ethylene, propylene and isoprene as described above.

RESULTS AND DISCUSSION

Measurement of Isoprene in Air

The Se-30 column in combination with GC-FID had shown to be simple and competent for measurement of isoprene in air. The advantage includes (1) easiness; (2) low cost; (3) quickness, with short retention times for ethylene and isoprene, and (4) directness, without tedious concentrators. Although it may not so sensitive as photoionization detector (PID)[11], it is really competent for screening the isoprene emitters when the PP bag enclosure method was applied in together.

When a 2 ppm of isoprene was prepared using ambient air of Taipei for dilution, the GC-FID spectrum was like the one in Fig 1. In addition to the isoprene peak

with retention time at 0.908 min, there is also an ethylene peak with retention time of 0.63 min which occurred frequently at Taipei.

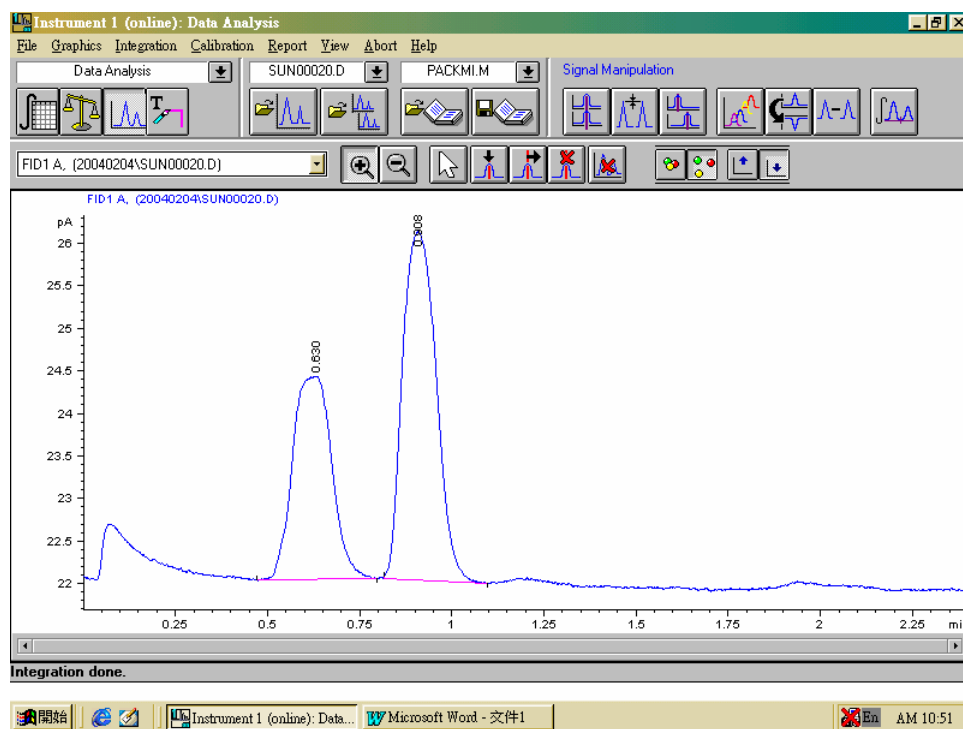


Fig. 1. Spectrum of 2 ppm isoprene as determined by GC-FID using a Se-30 column.

When the poongaoil (*Pongamia pinnata*) branch was enclosed in PP bag and the emission was measured with GC, the spectrum was like that in Fig. 2. There is always an ethylene peak coming to the spectrum as a dominant air contaminant in Taipei.

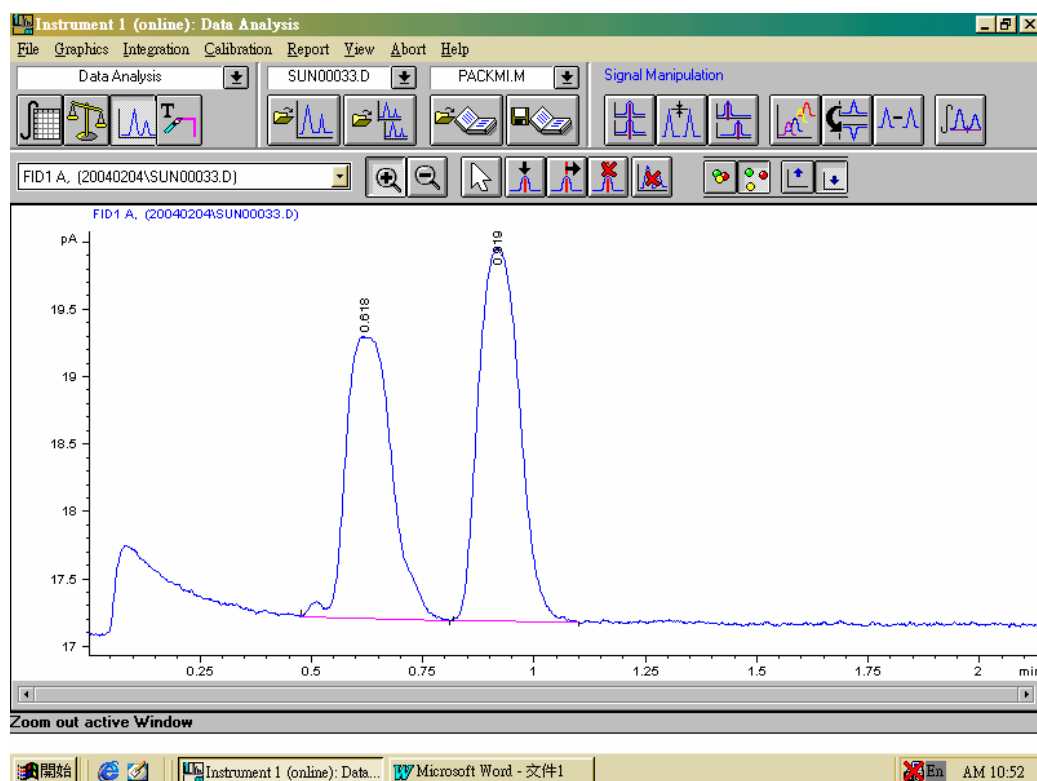


Fig. 2. Spectrum of isoprene emitted by poongaoil tree and ambient ethylene as determined by GC-FID using a Se-30 column.

Screening of Common Tree Species for Isoprene Emission in Taiwan

Totally 28 species of trees were screened for their isoprene emission. The results were shown in Table 1.

Table 1. Isoprene emission situation of 28 tree species in Taiwan as measured by branch enclosure method and determined with GC-FID using Se-30 column.

Order	Scientific name	Common name	Emission rate of isoprene (ug/g/h)	Emission grade*
01	<i>Bischofia javanica</i>	Red cedar	0	A
02	<i>Cinnamomum camphora</i>	Camphor	0	A
03	<i>Michelia compressa</i>	Formosan michelia	Trace	B
04	<i>Fraxinus formosana</i>	Formosan ash	0	A

05	<i>Swietenia macrophylla</i>	Honduras mahogany	0	A
06	<i>Pterocarpus indicus</i>	Rose wood	Trace	B
07	<i>Liquidambar formosana</i>	Formosan sweet gum	38.4	D
08	<i>Koelreuteria henryi</i>	Flame goldrain	0	A
09	<i>Dalbergia sissoo</i>	Sisso tree	41.4	D
10	<i>Terminalia catappa</i>	Indian almond	0	A
11	<i>Terminalia boivinii</i>		0	A
12	<i>Zelkova serrata</i>	Taiwan zelkova	0	A
13	<i>Melia azedarach</i>	China berry	0	A
14	<i>Pistacia chinensis</i>	Chinese pistache	0	A
15	<i>Acacia confusa</i>	Taiwan acacia	0	A
16	<i>Ficus benjamina</i>	White bark fig	27.7	D
17	<i>Pongamia pinnata</i>	Poongaoil	12.4	C
18	<i>Cassia fistula</i>	Golden shower	Trace	B
19	<i>Elaeocarpus serratus</i>	Celon olive	14.8	C
20	<i>Podocarpus nagi</i>	Nagi podocarp	0	A
21	<i>Podocarpus macrophyllus</i>	Yew podocarp	0	A
22	<i>Osmanthus fragrans</i>	Sweet osmanthus	Trace	B
23	<i>Mangifera indica</i>	Mango	39.5	D
24	<i>Cinnamomum micranthum</i>	Stout camphor	0	A
25	<i>Ficus elastica</i>	Rubber plant	21.1	D
26	<i>Calophyllum inophyllum</i>	Indiapoon beautyleaf	0	A
27	<i>Calocedrus formosana</i>	Taiwan incense cedar	0	A
28	<i>Palaquium formosanum</i>	Formosan nato	Trace	B

*Emission grade: A = No emission; B = Trace; C = medium; D = High

From the data in Table 1, we can find that seven among 28 species were isoprene emitters. They are mango, Formosan sweet gum (*Liquidambar formosana*), sisso tree (*Dalbergia sissoo*), white bark fig (*Ficus benjamina*), rubber plant (*Ficus*

elastica), poongaoil (*Pongamia pinnata*), and Ceylon olive (*Elaeocarpus serratus*), with emission rate of 39.5, 38.4, 41.4, 27.7, 21.1, 12.4, and 14.8 $\mu\text{g g}^{-1} \text{h}^{-1}$, respectively.

The results suggest that these species should be avoided or limited in urban reforestation, although there is no direct evidence showing that the emitted isoprene is the principal precursor responsible for the raised ozone level in four urban areas in Taiwan.

Comparison between Ambient Concentrations of Ethylene, propylene and Isoprene

As those shown in Fig. 1 and 2, ethylene was a major air contaminant whenever the isoprene was determined at Taipei. Sometimes we can also detect high concentrations of propylene as shown in Fig. 3.

For most of the time we found that ethylene and propylene were dominant species, while the isoprene was not detectable. Therefore we think that the isoprene emitted by green plants in Taipei is not playing an important role in increasing ozone concentration in the air. All these VOC molecules contained double-bond, and were recognized as ozone precursors as they were very reactive in photochemical reaction. However, we found that the isoprene concentration is usually lower than the other two species. On the other side, occurrence of ethylene and propylene in Taipei urban areas seemed to be an important problem as they may play important roles in forming the ozone.

Isoprene was thought to react with ozone and remove ozone when there was no anthropogenic pollutants such as nitrogen oxides[31]. Based on this fact, the emission of isoprene in mountain areas would be not a problem for

increasing ozone concentration.

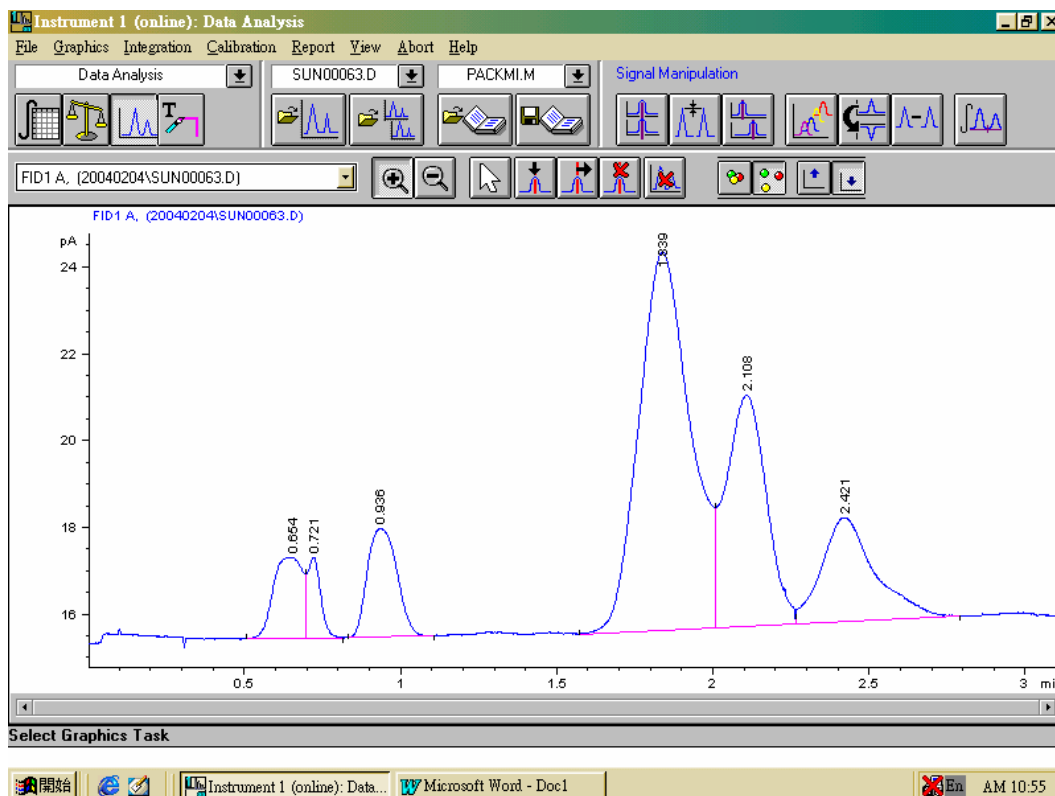


Fig. 3. Spectrum of isoprene ($R_t = 0.936$) emitted by white bark fig together with ambient ethylene ($R_t = 0.654$), propylene ($R_t = 0.721$) and three other PP bag contaminants ($R_t > 1.9$) as determined by GC-FID using a Se-30 column.

CONCLUSION

In this study, we found: (1) The Se-30 column in combination with GC-FID had shown to be simple and competent for measurement of isoprene in air. (2) Screening results showed that seven among 28 species in Taiwan were isoprene emitters. They are mango, Formosan sweet gum (*Liquidambar formosana*), sisso tree (*Dalbergia sissoo*), white bark fig (*Ficus benjamina*), rubber plant (*Ficus elastica*), poongaoil (*Pongamia pinnata*), and Ceylon olive (*Elaeocarpus serratus*). (3) We found that ethylene and propylene were dominant species in Taipei atmosphere, while

isoprene was usually not detectable. (4) The occurrence of ethylene and propylene, but not the isoprene in Taipei urban areas, seemed to play an important role in forming the ozone.

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