Characterization of isoprene and its oxidation products at a remote subtropical forested mountain site, South China

Daocheng Gong, Hao Wang, Boguang Wang*, etc.

Institute for Environmental and Climate Research

Jinan University, Guangzhou

hjgc2012@yeah.net

June 5, 2017

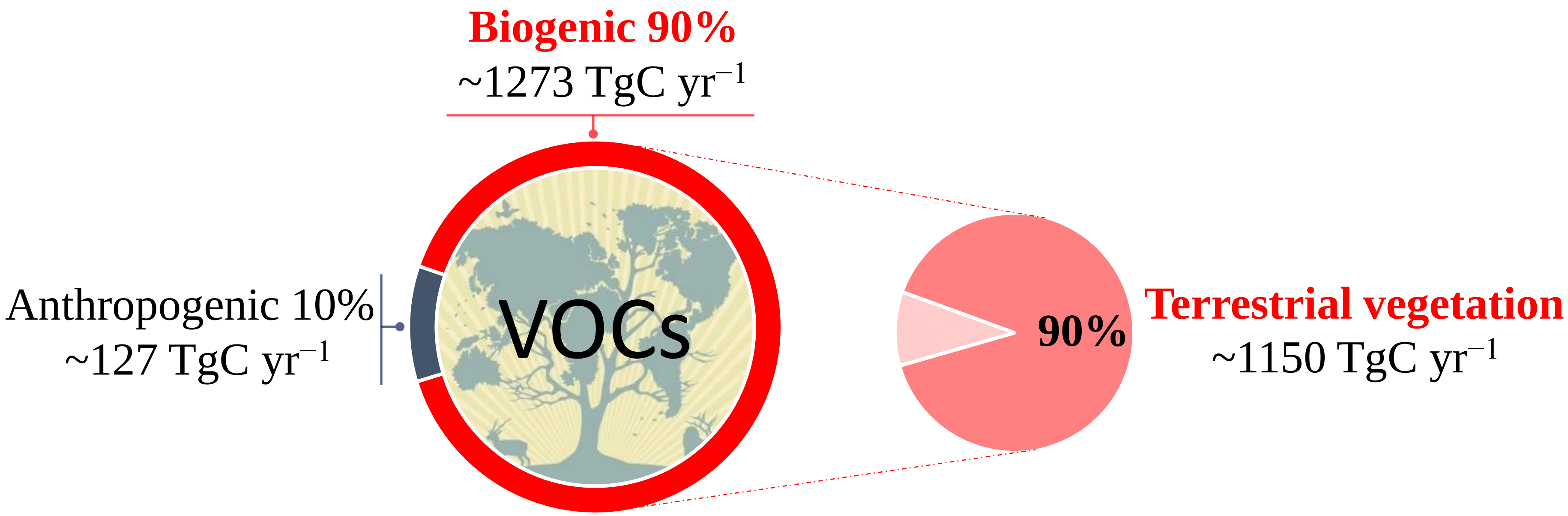
Contents

Contents

BVOCs

Biogenic volatile organic compounds (BVOCs):

the most abundant VOCs in the troposphere.

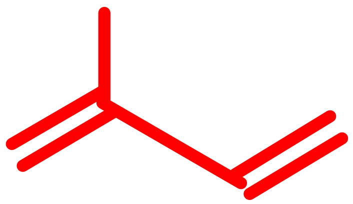


Dominant source of BVOCs:

terrestrial vegetation (mainly trees and shrubs).

Guenther et al., 1995, 2012; Steiner and Goldstein, 2007; Olivier Boucher et al., 2013.

Isoprene



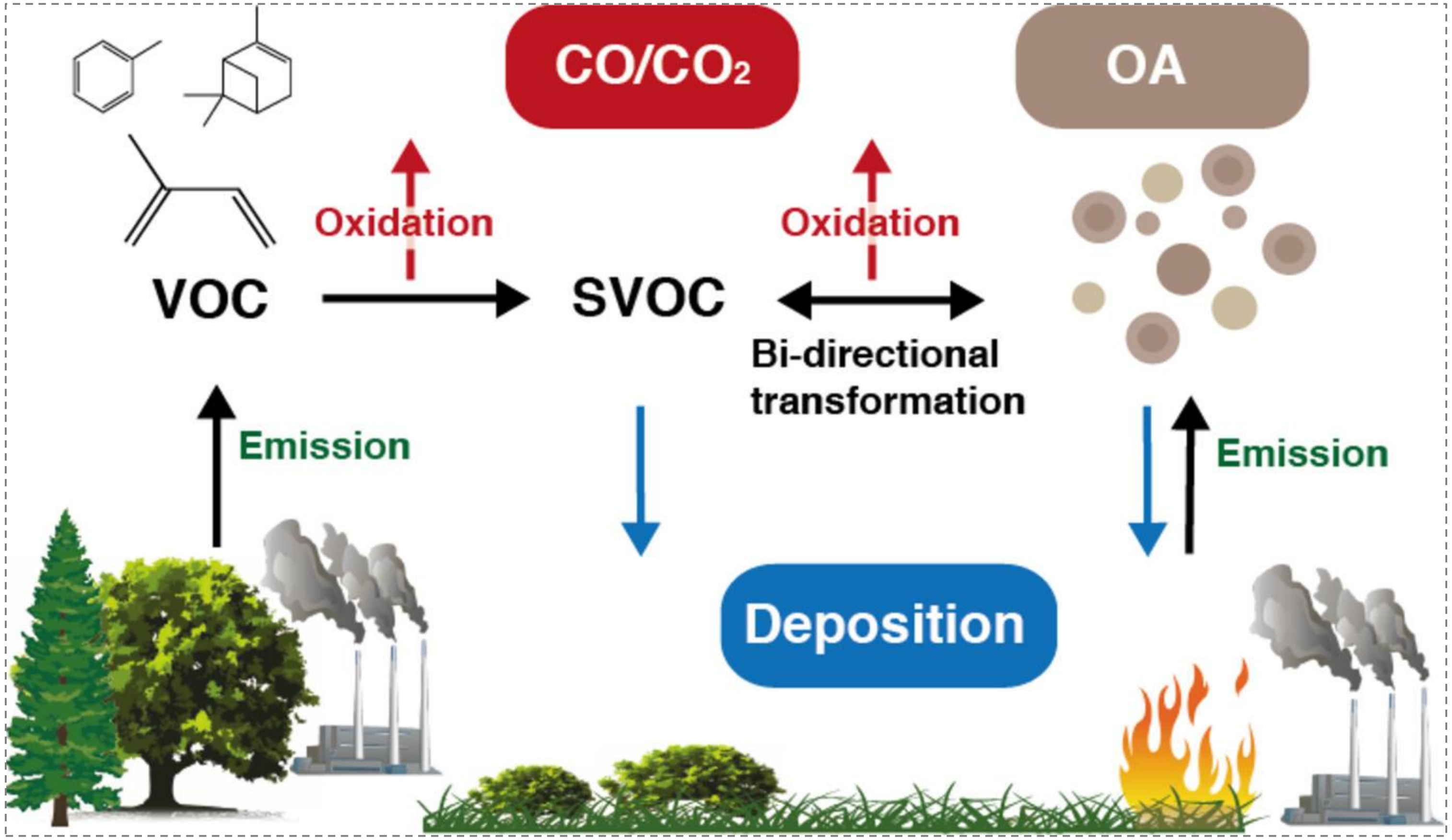
the predominant BVOC (~53%),

the largest single species of VOCs in the atmosphere.

Guenther et al., 1995, 2012.

Atmospheric implications of isoprene

Isoprene is highly reactive: has important implications for the oxidative capacity of the atmosphere, the local and regional air quality and even the global climate change.



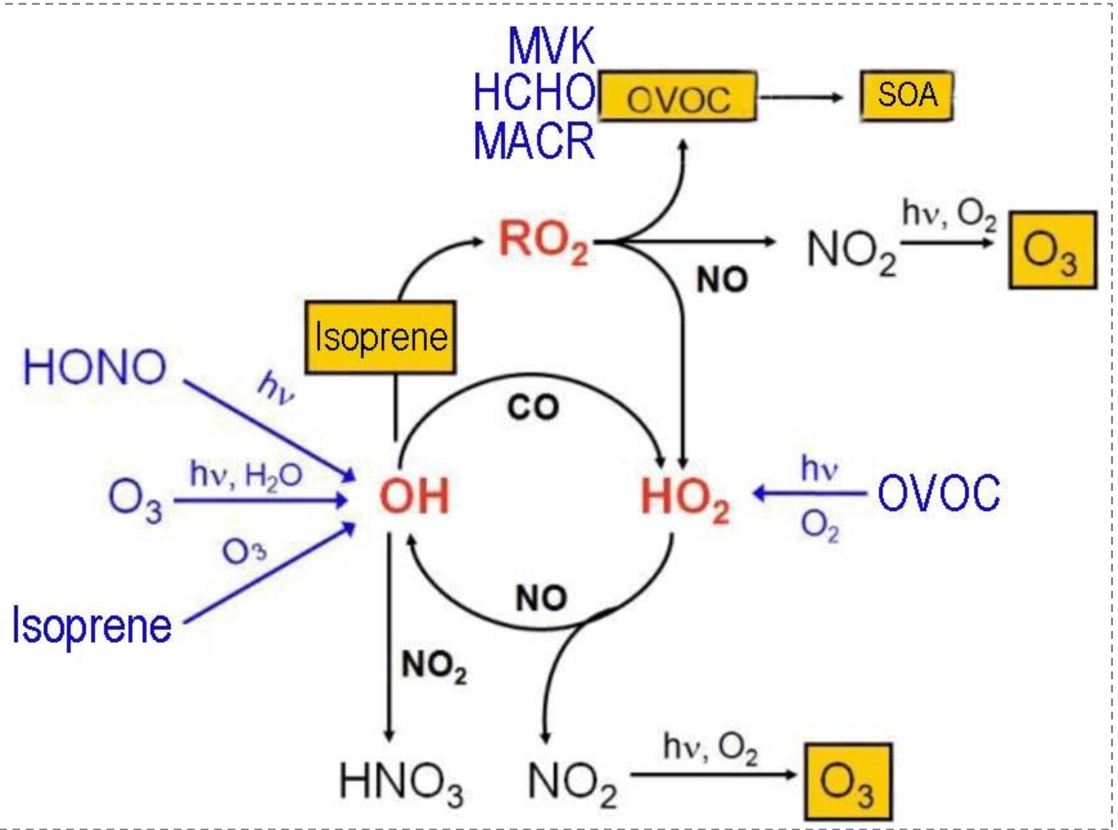
Glasius, M. and A.H. Goldstein, EST, 2016.

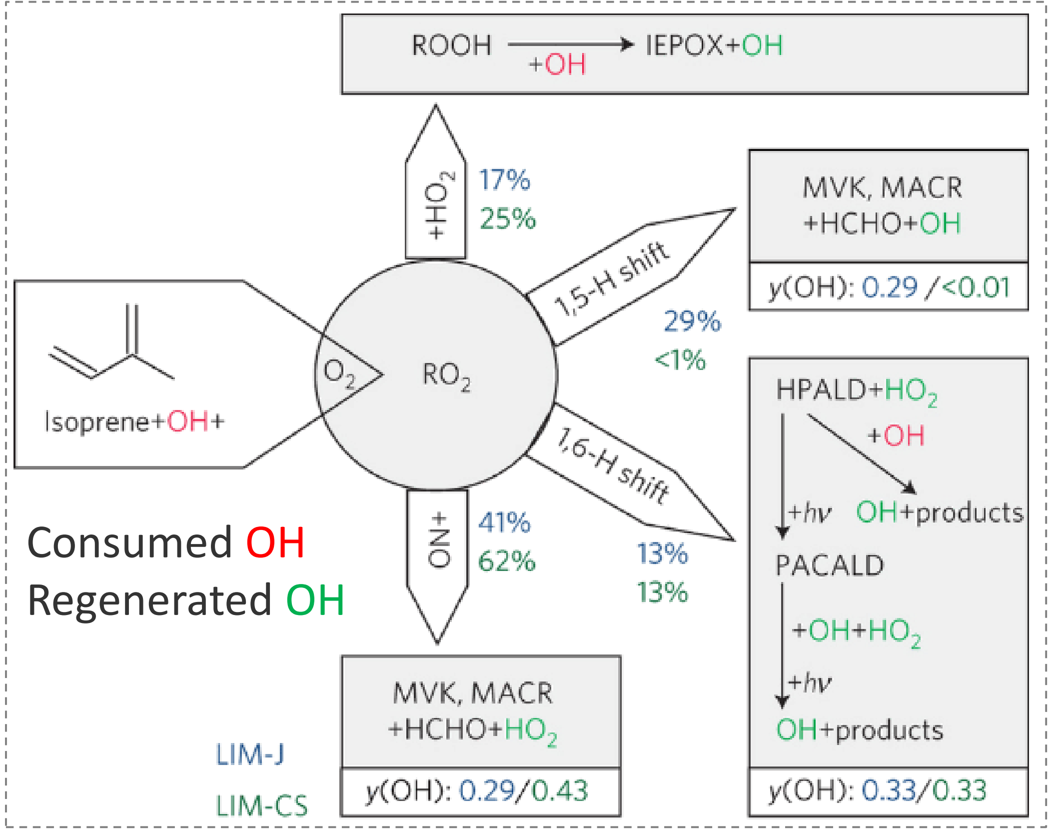
High OH in forested regions

Daytime isoprene oxidation with OH radical:

high OH concentrations were observed in isoprene-rich and NO-rare forests

due to OH regeneration and recycling.



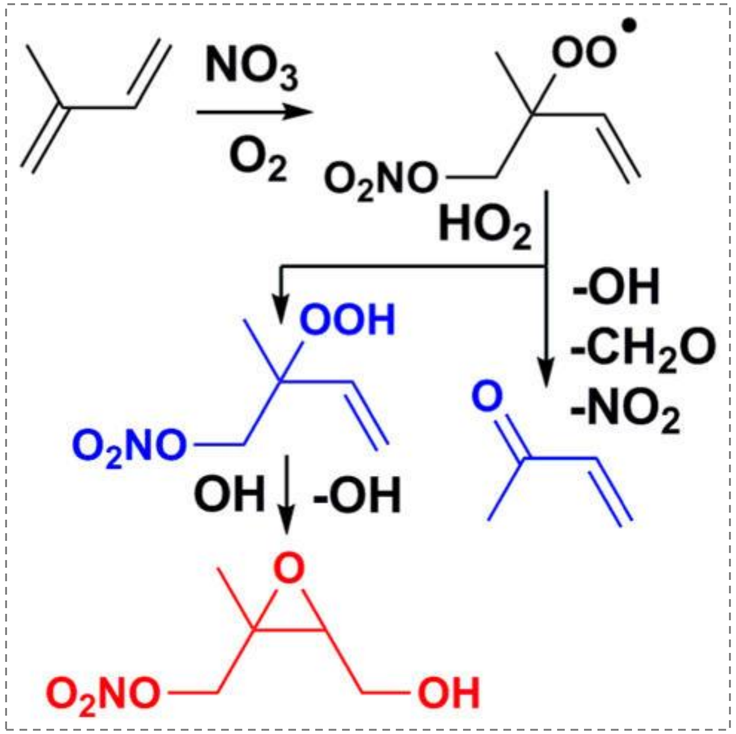


Nighttime chemistry of isoprene

Nocturnal isoprene oxidation with NO_3 radical:

specifically important in polluted atmospheres with high levels of O_3 and NO_2.

$$NO_2 + O_3 \rightarrow NO_3$$

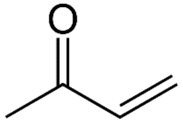
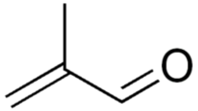


Schwantes, R.H., et al., 2015;Brown et al., 2016;Millet et al., 2016.

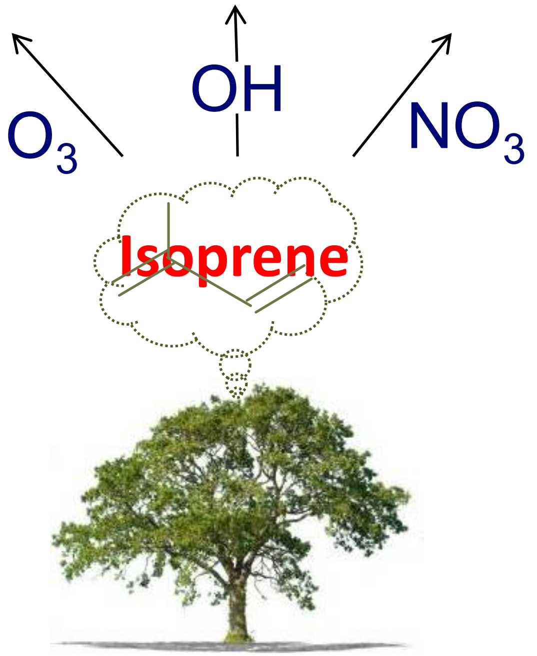
Key intermediates of isoprene oxidation

Methyl vinyl ketone (MVK) and methacrolein (MACR):

major intermediates generated from isoprene oxidation with OH, NO_3 and O_3.

 MVK+MACR 

80% of the carbon in the initial oxidation of isoprene



Lelieveld et al., 2008;Atkinson et al., 2006;Fuchs et al., 2013;Peeters et al., 2009;Millet et al., 2016; Karl et al., 2010;Xu et al., 2015.

Brief summary

Large emission rates and high reactivity make isoprene particularly important in local and regional air chemistry, especially in highly polluted atmospheres.

Measurment of isoprene, MVK and MACR is an effective way to better understand the role that isoprene plays in the atmosphere.

Table 1 Rate constants and lifetime for isoprene, MVK and MACR, and yields of MVK and MACR from the isoprene reactions

Compound	Rate constants[a] with			Yield[b] from isoprene reaction with / (life time[b] for reaction with)		
	OH	NO_3	O_3	OH	NO_3	O_3
Isoprene	1.0×10^{-10}	7.0×10^{-13}	1.3×10^{-17}	-/ 1.4 h	-/ 1.6 h	-/ 1.3 d
MVK	2.0×10^{-11}	6.0×10^{-16}	5.2×10^{-18}	0.33 / 6.9 h	0.035 / 2.1 y	0.16 / 3.4 d
MACR	2.9×10^{-11}	3.4×10^{-15}	1.2×10^{-18}	0.23 / 4.8 h	0.035 / 28 d	0.41 / 15 d

[a] (Atkinson et al., 2006) and references therein, unit in cm^3 $molecules^{-1}$ s^{-1}, temperature in 298 K.

[b] (Atkinson and Arey, 2003) and references therein. Assumed OH radical, NO_3 radical and O_3 concentrations: 2.0×10^6, 2.5×10^8 and 7.0×10^{11} molecule cm^{-3}, 12-h daytime, 12-h nighttime and 24-h average, respectively.

Atkinson et al., 2006; Atkinson and Arey, 2003.

Aim & Objectives

To improve the understanding of the isoprene chemistry

in polluted regions of strong atmospheric oxidative capacity.

Contents

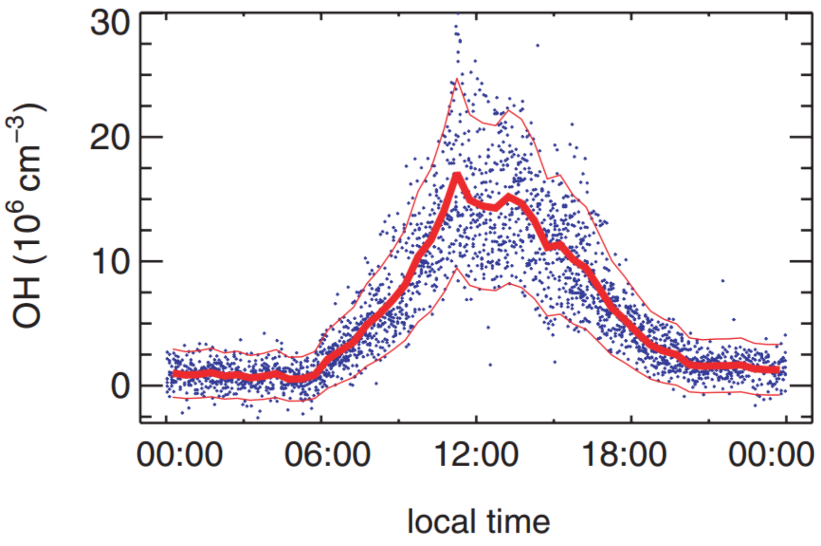
PRD

The Pearl River Delta (PRD) region is one of the most air-polluted areas in China:

high OH, O_3 and NO_2 levels, strong atmospheric oxidative capacity.

Site	Month, year	OH[a] (10^6 cm^{-3})	Reference
Los Angeles (34° N)	Sep 1993	5–7	George et al. (1999)
Berlin (52.9° N)	Jul–Aug 1998	4–8	Holland et al. (2003)
Birmingham (52.4° N)	Jun 1999	2–9	Emmerson et al. (2005)
Nashville (36.2° N)	Jun–Jul 1999	7.5–20	Martinez et al. (2003)
New York City[f] (40.7° N)	Jun–Aug 2001	3–33	Ren et al. (2003)
Mexico City[f,g] (19.4° N)	Apr 2003	8–13	Shirley et al. (2006)
London (51.7° N)	Jul–Aug 2003	1–6	Emmerson et al. (2007)
Tokyo (35.6° N)	Jul–Aug 2004	5–13	Kanaya et al. (2007b)
Houston (29.7° N)	Aug 2000	≈18	Mao et al. (2010)
Houston (29.7° N)	Sep 2006	≈14	Mao et al. (2010)
Guangzhou (23.5° N)	Jul 2006	15–26	Lu, K.D., et al. (2012)

Noontime maxima of measured HO_x concentrations at urban and suburban sites during summer time.

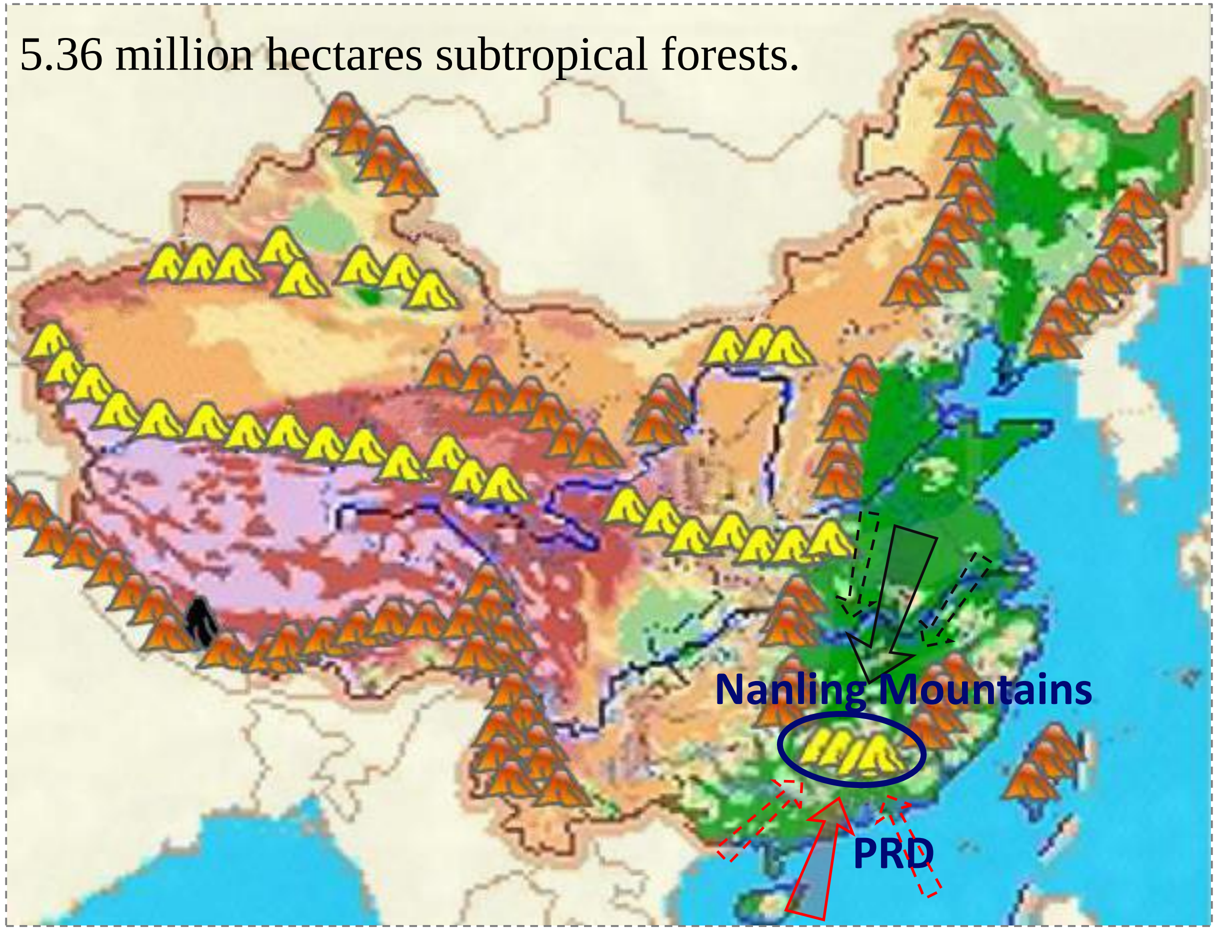


Chan and Yao, 2008; Hofzumahaus, A., et al., 2009;Lu, K.D., et al., 2012; Xue, L.K., et al., 2016.

Nanling Mountains

Natural barrier of Guangdong; key pathway for the long-range transport of air pollutants.

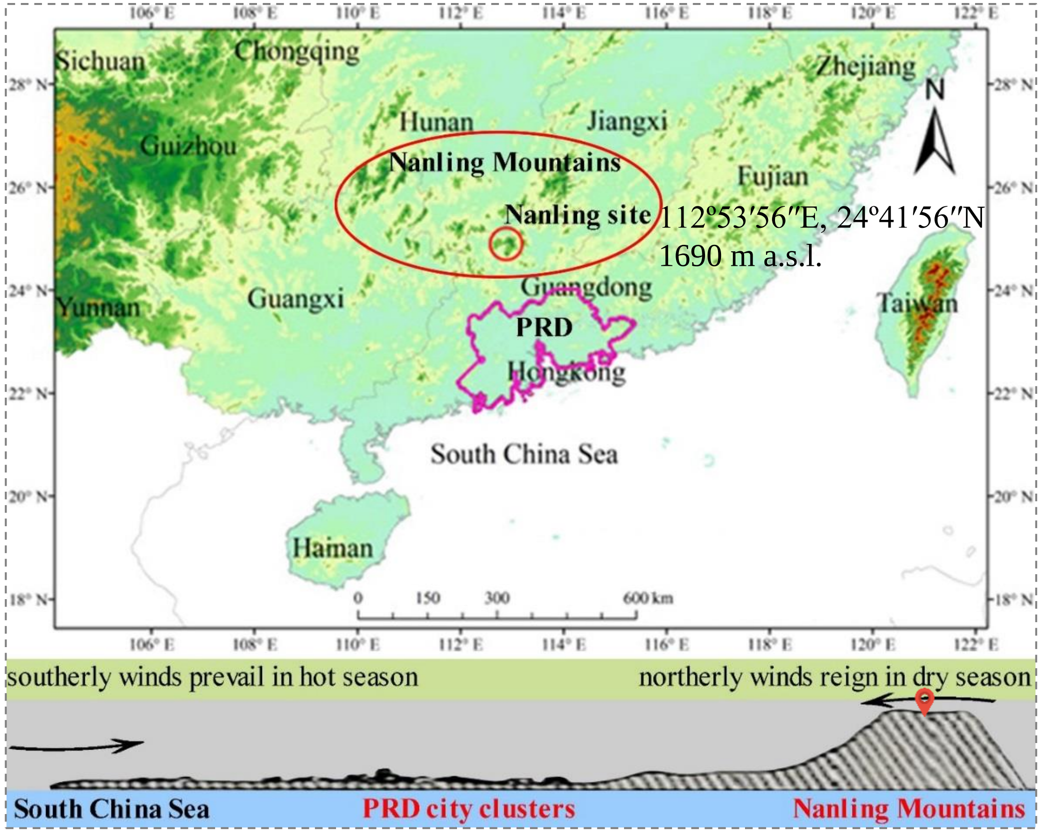
No isoprene measurements have been conducted in this important area.



Site description

Nanling site: a remote subtropical forested high-altitude (1690 m a.s.l.) mountain site.

The forest nearby is mainly composed of subtropical evergreen broad-leaved trees and Moso bamboo, both of which are strong isoprene emitters.



Wu, et al., 2016; Klinger et al., 2002; Bai et al., 2016; Guenther et al., 2012.

Instrumentation

Real-time and continuous measurements achieved automatically by an online cryogen-free GC–MS system in hot season (July 15th – Aug. 17th 2016).

Wang et al., 2014; Li et al., 2016.

OH and NO_3 calculating

"Back-of-the-envelope" approach: [MVK+MACR]/[Isoprene] = *f* ([reactants]).

[OH] and [NO_3] can be obtained by equations solving.

$$\left(\frac{\partial[\mathrm{ISO}]}{\partial t}\right)_{\mathrm{Daytime}} = -(k_{\mathrm{ISO,OH}} \times [\mathrm{OH}] + k_{\mathrm{ISO,O_3}} \times [\mathrm{O_3}]) \times [\mathrm{ISO}]$$

$$\left(\frac{\partial[\mathrm{ISO}]}{\partial t}\right)_{\mathrm{Nighttime}} = -(k_{\mathrm{ISO,NO_3}} \times [\mathrm{NO_3}] + k_{\mathrm{ISO,O_3}} \times [\mathrm{O_3}]) \times [\mathrm{ISO}]$$

$$\left(\frac{\partial[\mathrm{MVK}]}{\partial t}\right)_{\mathrm{Daytime}} = y_{\mathrm{MVK,OH}} \times \left(\frac{\partial[\mathrm{ISO}]}{\partial t}\right)_{\mathrm{OH}} + y_{\mathrm{MVK,O_3}} \times \left(\frac{\partial[\mathrm{ISO}]}{\partial t}\right)_{\mathrm{O_3}} - (k_{\mathrm{MVK,OH}} \times [\mathrm{OH}] + k_{\mathrm{MVK,O_3}} \times [\mathrm{O_3}]) \times [\mathrm{MVK}]$$

$$\left(\frac{\partial[\mathrm{MACR}]}{\partial t}\right)_{\mathrm{Daytime}} = y_{\mathrm{MACR,OH}} \times \left(\frac{\partial[\mathrm{ISO}]}{\partial t}\right)_{\mathrm{OH}} + y_{\mathrm{MACR,O_3}} \times \left(\frac{\partial[\mathrm{ISO}]}{\partial t}\right)_{\mathrm{O_3}} - (k_{\mathrm{MACR,OH}} \times [\mathrm{OH}] + k_{\mathrm{MACR,O_3}} \times [\mathrm{O_3}]) \times [\mathrm{MACR}]$$

$$\left(\frac{\partial[\mathrm{MVK}]}{\partial t}\right)_{\mathrm{Nighttime}} = y_{\mathrm{MVK,NO_3}} \times \left(\frac{\partial[\mathrm{ISO}]}{\partial t}\right)_{\mathrm{NO_3}} + y_{\mathrm{MVK,O_3}} \times \left(\frac{\partial[\mathrm{ISO}]}{\partial t}\right)_{\mathrm{O_3}} - (k_{\mathrm{MVK,NO_3}} \times [\mathrm{NO_3}] + k_{\mathrm{MVK,O_3}} \times [\mathrm{O_3}]) \times [\mathrm{MVK}]$$

$$\left(\frac{\partial[\mathrm{MACR}]}{\partial t}\right)_{\mathrm{Nighttime}} = y_{\mathrm{MACR,NO_3}} \times \left(\frac{\partial[\mathrm{ISO}]}{\partial t}\right)_{\mathrm{NO_3}} + y_{\mathrm{MACR,O_3}} \times \left(\frac{\partial[\mathrm{ISO}]}{\partial t}\right)_{\mathrm{O_3}} - (k_{\mathrm{MACR,NO_3}} \times [\mathrm{NO_3}] + k_{\mathrm{MACR,O_3}} \times [\mathrm{O_3}]) \times [\mathrm{MACR}]$$

Karl et al., 2007; Kuhn et al., 2007; Atkinson et al., 2006.

Atmospheric lifetime estimating

$$\frac{[\text{MVK}]/[\text{Isoprene}]}{[\text{MACR}]/[\text{Isoprene}]} = f\,([\text{OH}], t) \text{ or } f\,([\text{NO}_3], t).$$

Lifetime t can be expected by compare this theoretical curve with actual data.

$\text{Isoprene} + \text{OH} \rightarrow 0.23\,\text{MACR} + 0.33\,\text{MVK}$	$k_1 = 1.0 \times 10^{-10}$
$\text{MACR} + \text{OH} \rightarrow \text{products}$	$k_2 = 2.9 \times 10^{-11}$
$\text{MVK} + \text{OH} \rightarrow \text{products}$	$k_3 = 2.0 \times 10^{-11}$
$\text{Isoprene} + \text{NO}_3 \rightarrow 0.035\,\text{MACR} + 0.035\,\text{MVK}$	$k_4 = 7.0 \times 10^{-13}$
$\text{MACR} + \text{NO}_3 \rightarrow \text{products}$	$k_5 = 3.4 \times 10^{-15}$
$\text{MVK} + \text{NO}_3 \rightarrow \text{products}$	$k_6 = 6.0 \times 10^{-16}$

$$\left(\frac{[\text{MACR}]}{[\text{Isoprene}]}\right)_{Daytime} = \frac{0.23k_1}{(k_2 - k_1)}(1 - e^{(k_1 - k_2)*[\text{OH}]_{avg}*t}) \qquad \left(\frac{[\text{MACR}]}{[\text{Isoprene}]}\right)_{Nighttime} = \frac{0.035k_4}{(k_5 - k_4)}(1 - e^{(k_4 - k_5)*[\text{NO}_3]_{avg}*t})$$

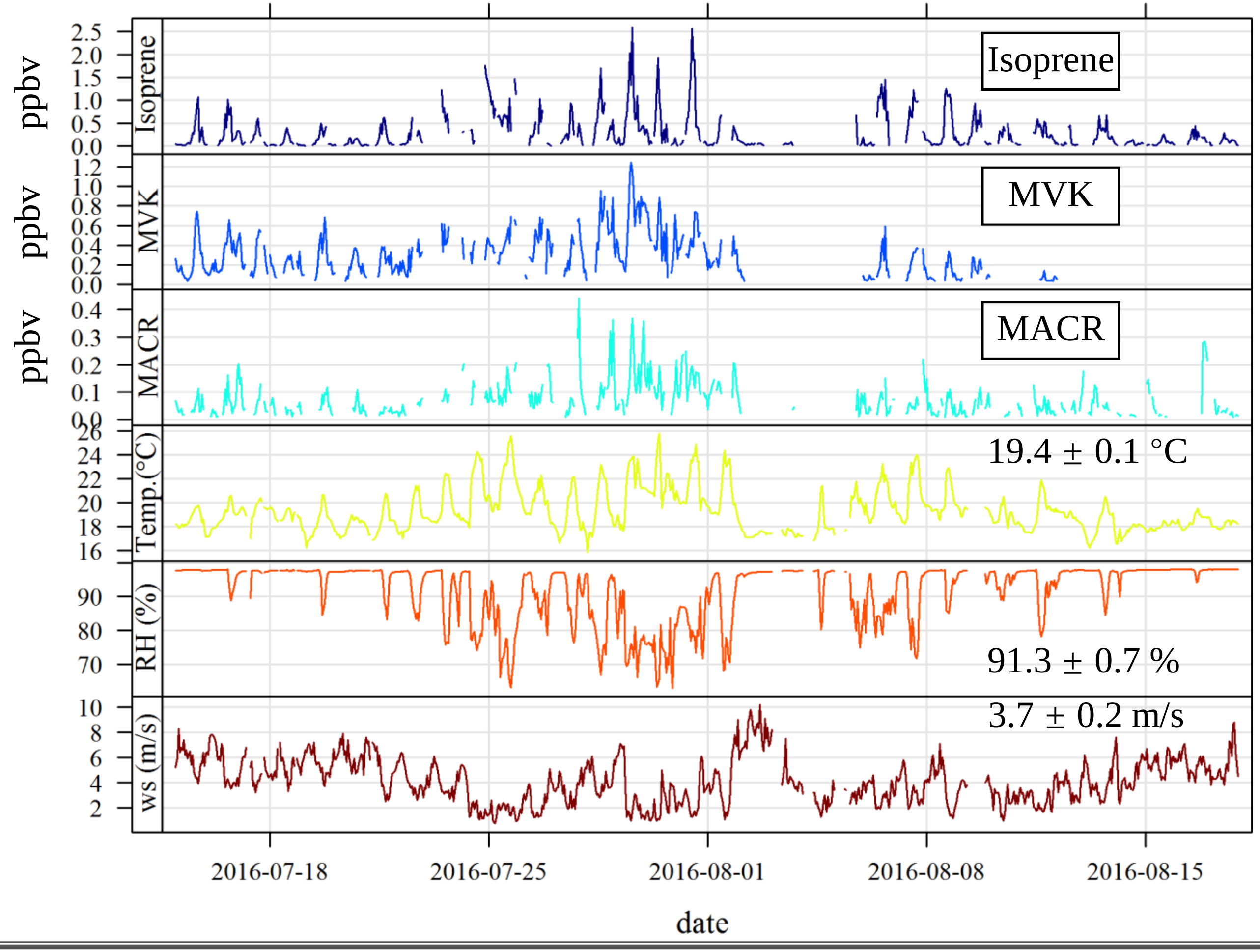
$$\left(\frac{[\text{MVK}]}{[\text{Isoprene}]}\right)_{Daytime} = \frac{0.32k_1}{(k_3 - k_1)}(1 - e^{(k_1 - k_3)*[\text{OH}]_{avg}*t}) \qquad \left(\frac{[\text{MVK}]}{[\text{Isoprene}]}\right)_{Nighttime} = \frac{0.035k_4}{(k_6 - k_4)}(1 - e^{(k_4 - k_6)*[\text{NO}_3]_{avg}*t})$$

Carter, 1996; Stroud et al., 2001.

Contents

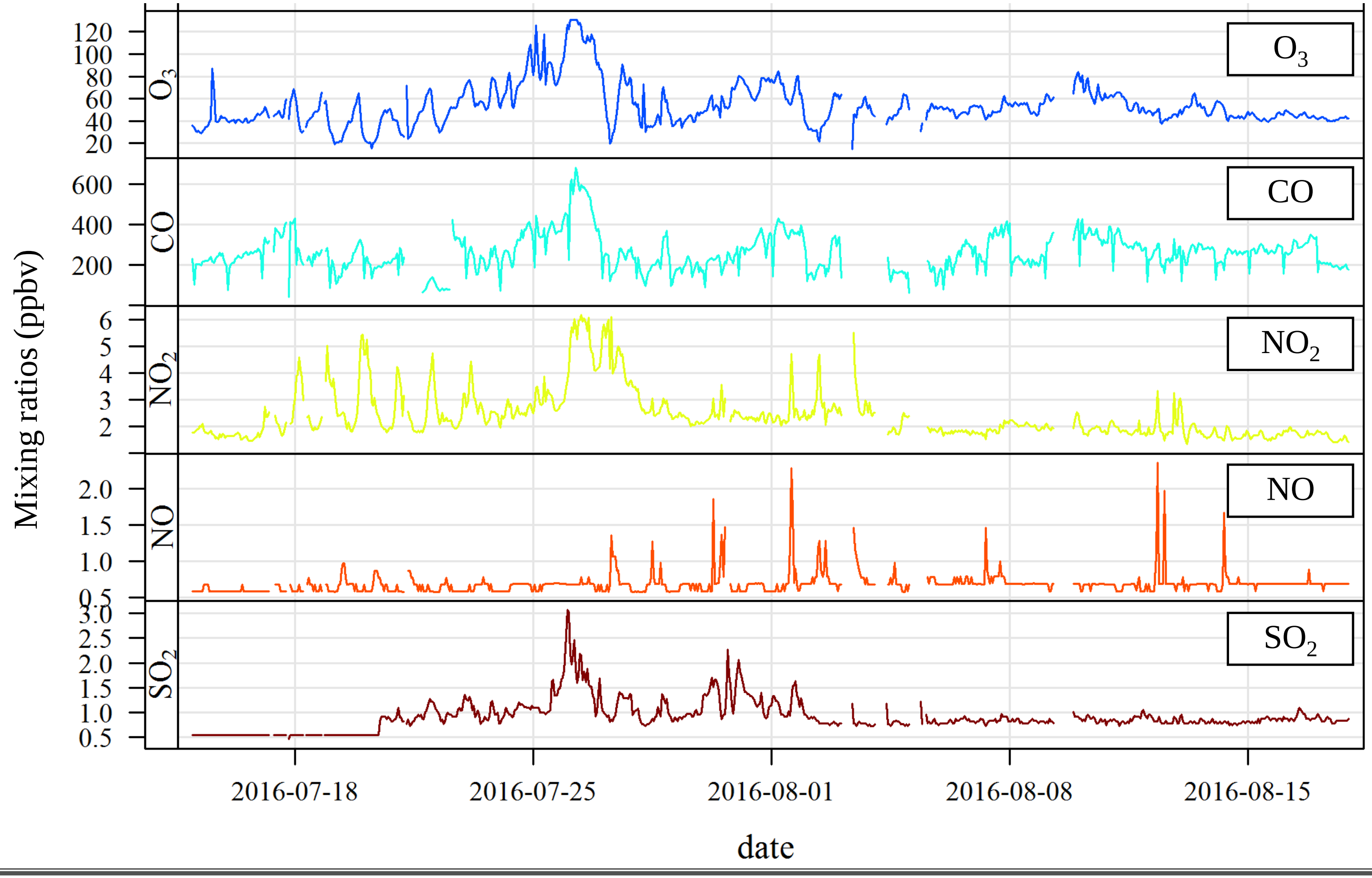
Overall concentrations

Average isoprene, MVK and MACR levels were 0.312, 0.300 and 0.073 ppbv, with a range of 0.004~2.605, 0.032~1.244 and 0.010~0.442 ppbv, respectively.



Overall concentrations

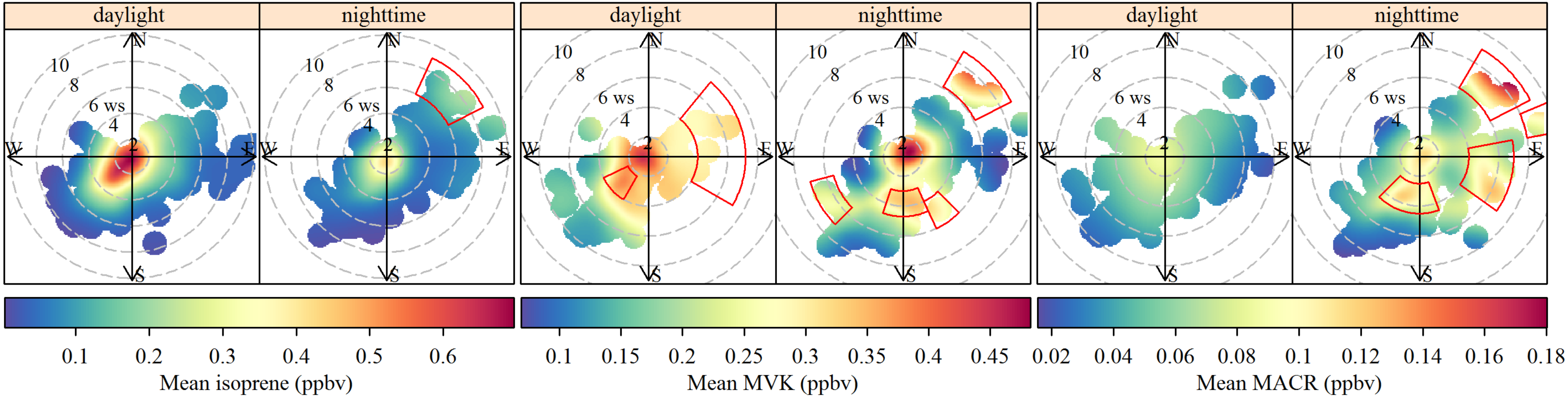
High levels of nighttime O_3 (56.960±2.160 ppbv), NO_2 (2.562±0.103 ppbv) and low NO (0.688±0.057 ppbv) were observed.



Graphical source identification

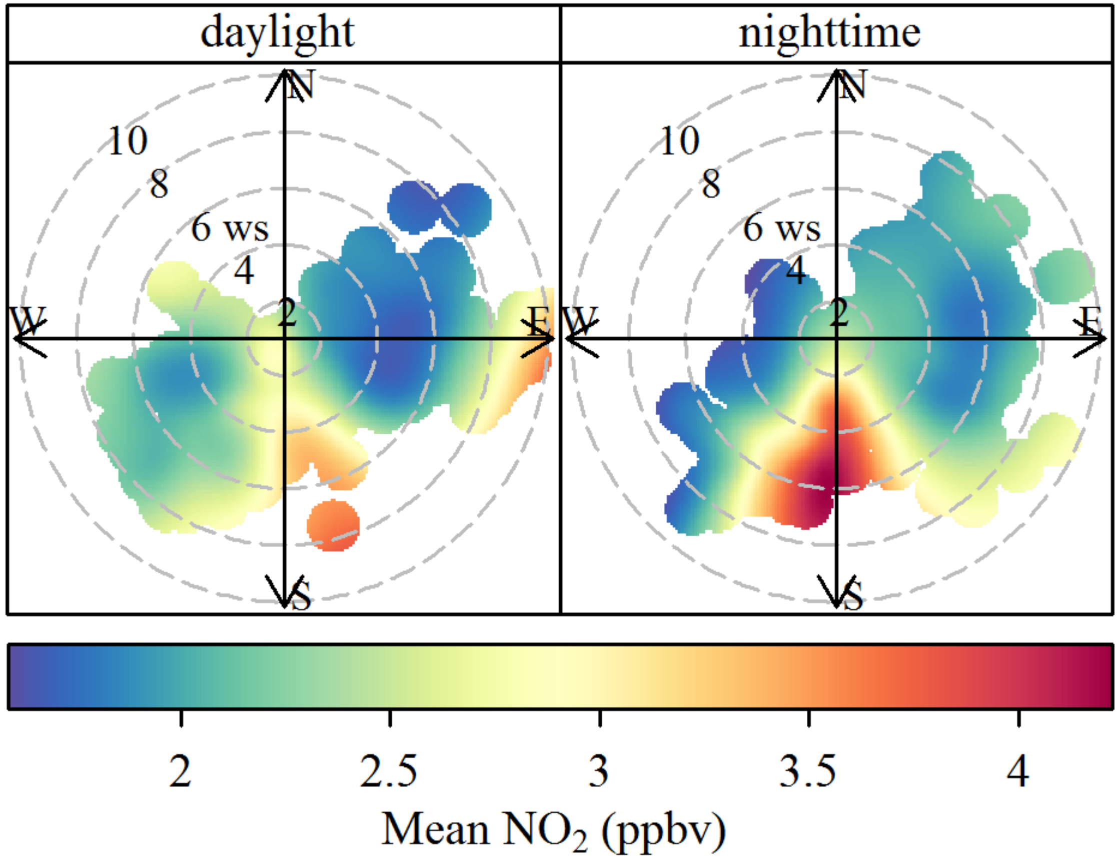
Isoprene: mainly local emissions.

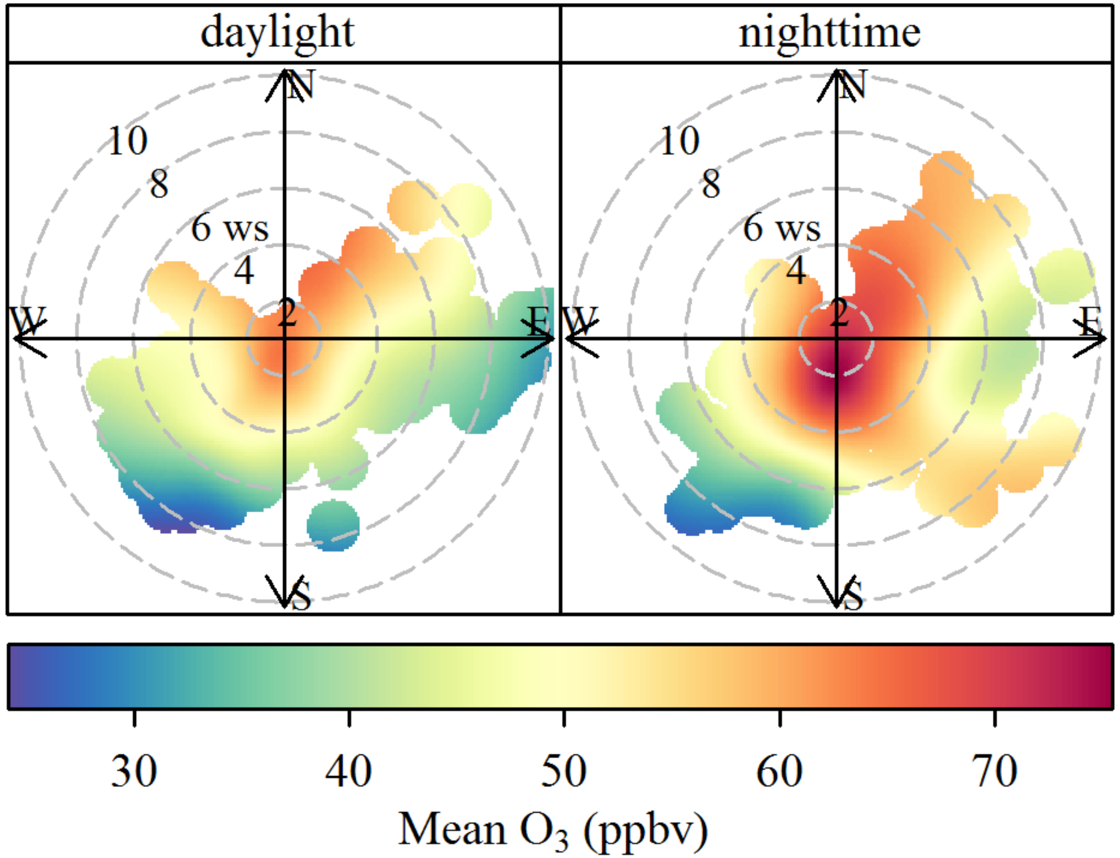
Transport interferences of anthropogenic MVK and MACR sources (motor vehicles and industrial sources) were identified as concentrations increased with increasing wind speed.



Nocturnal NO_3 formation

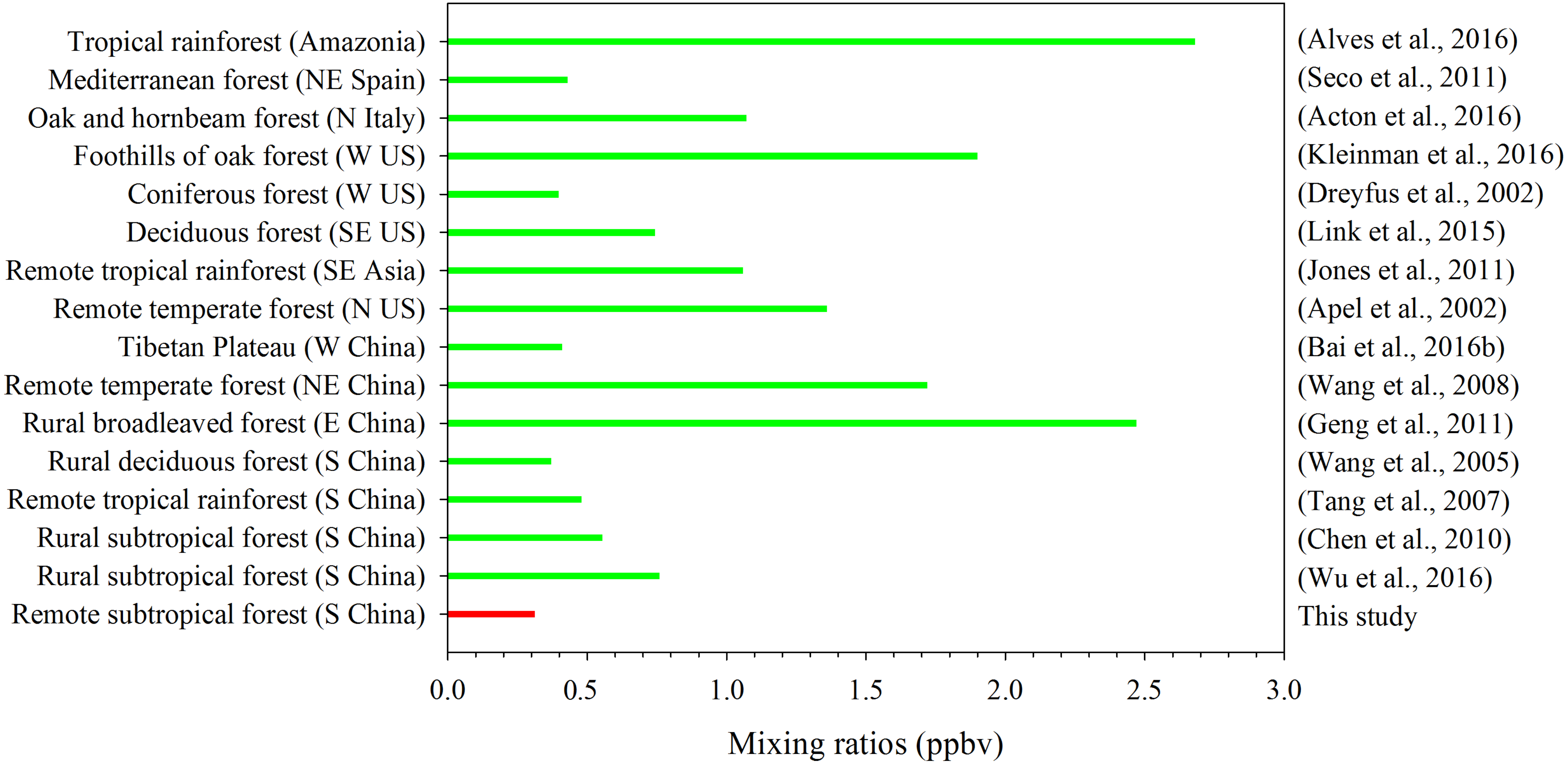
Nighttime southern NO_2 and local O_3 were favorable to the NO_3 formation.





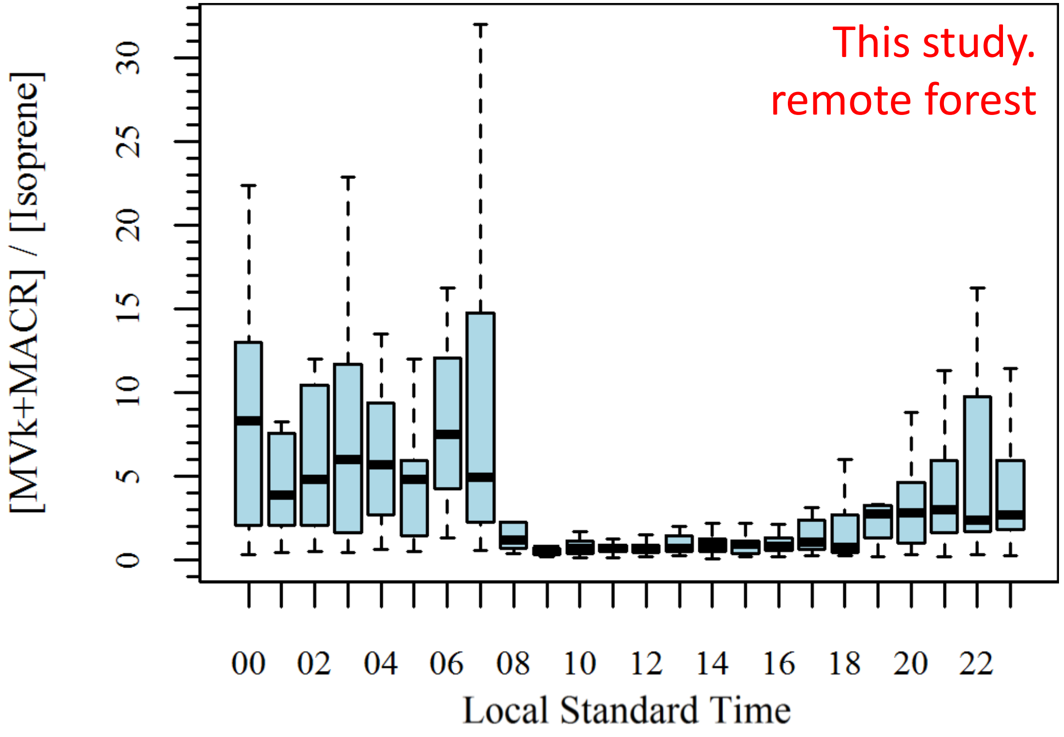
Low observed isoprene concentrations

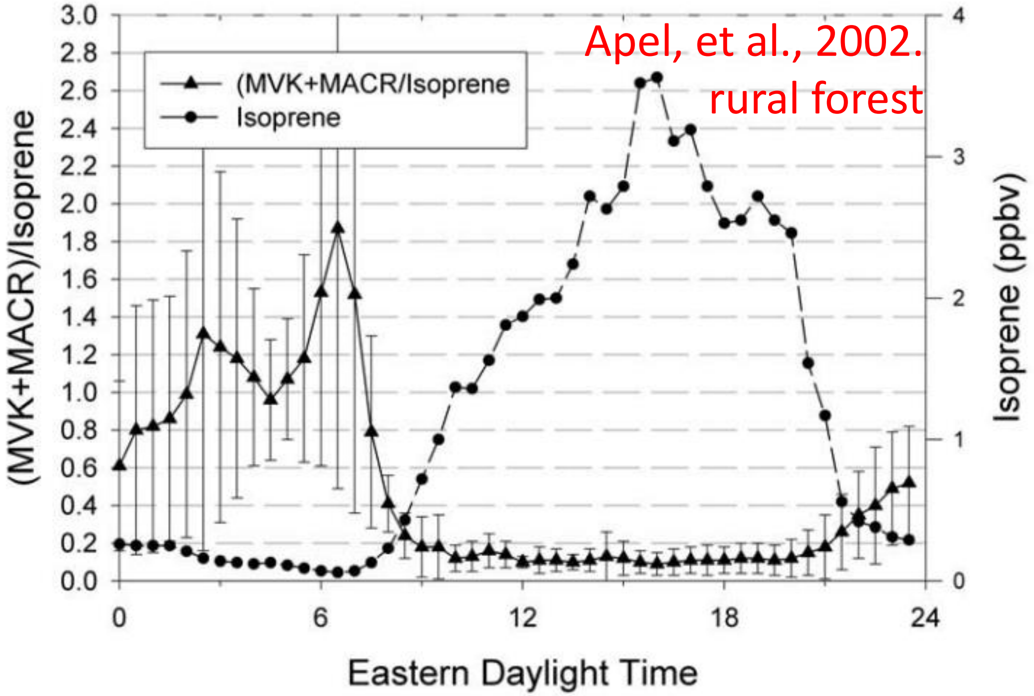
The isoprene levels in this study is lower than that observed in other background sites either in China or around the world.



High [MVK+MACR]/[Isoprene] ratios

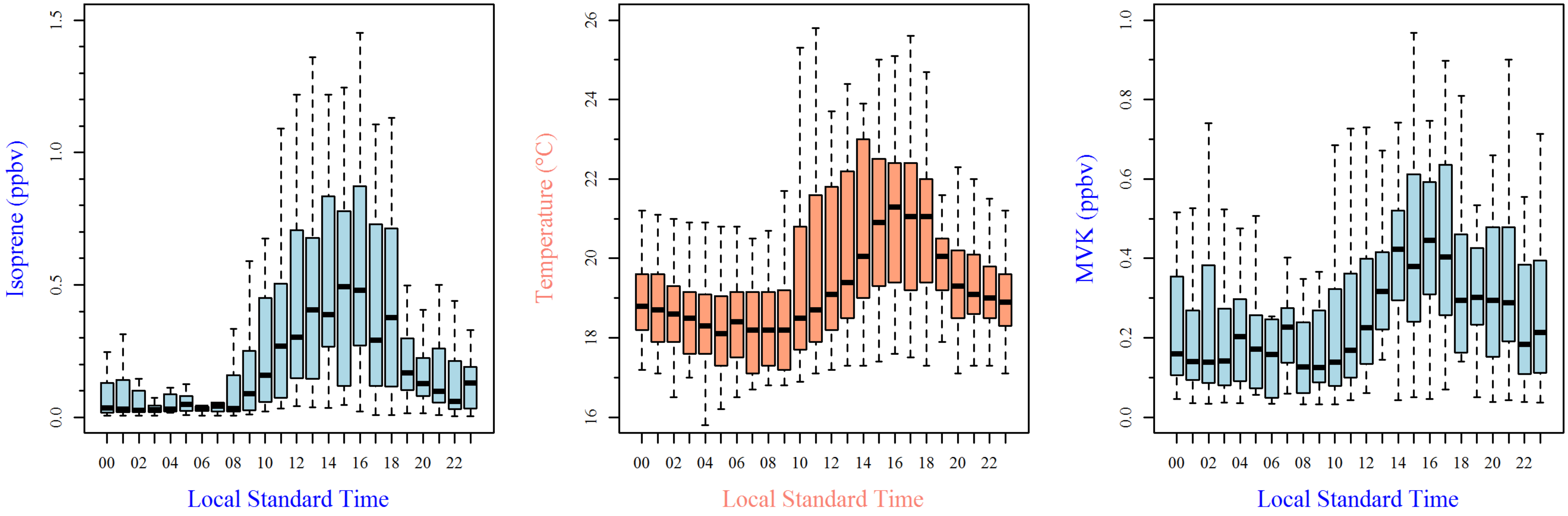
The [MVK+MACR]/[Isoprene] ratios observed were quite high both in nighttime (6.499± 1.499) and daytime (1.654 ± 0.503) hours, suggesting that both the isoprene in daytime and nighttime were fully oxidized.





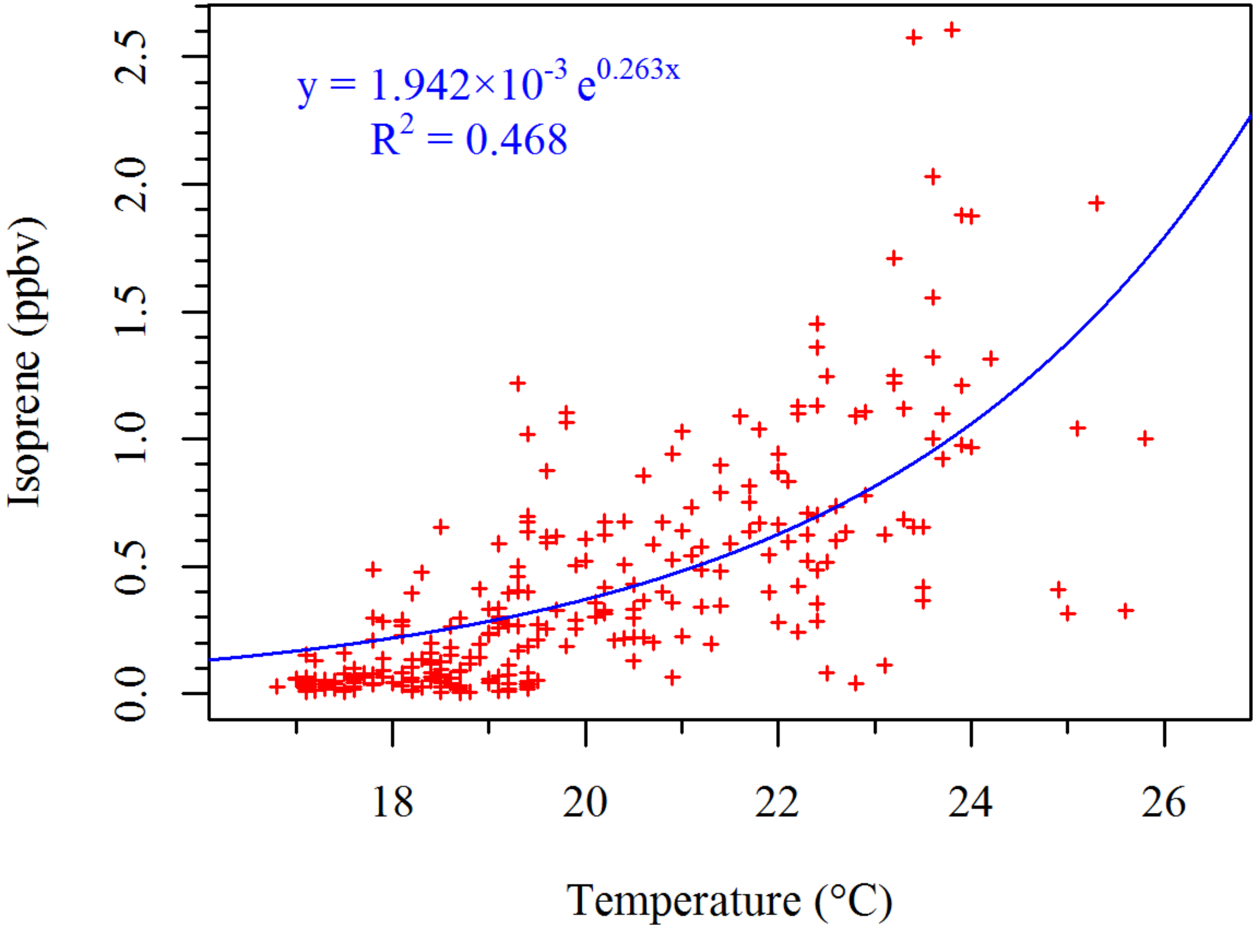
Diurnal variations

Isoprene and MVK peaked at 4 p.m., in accordance with temperature.



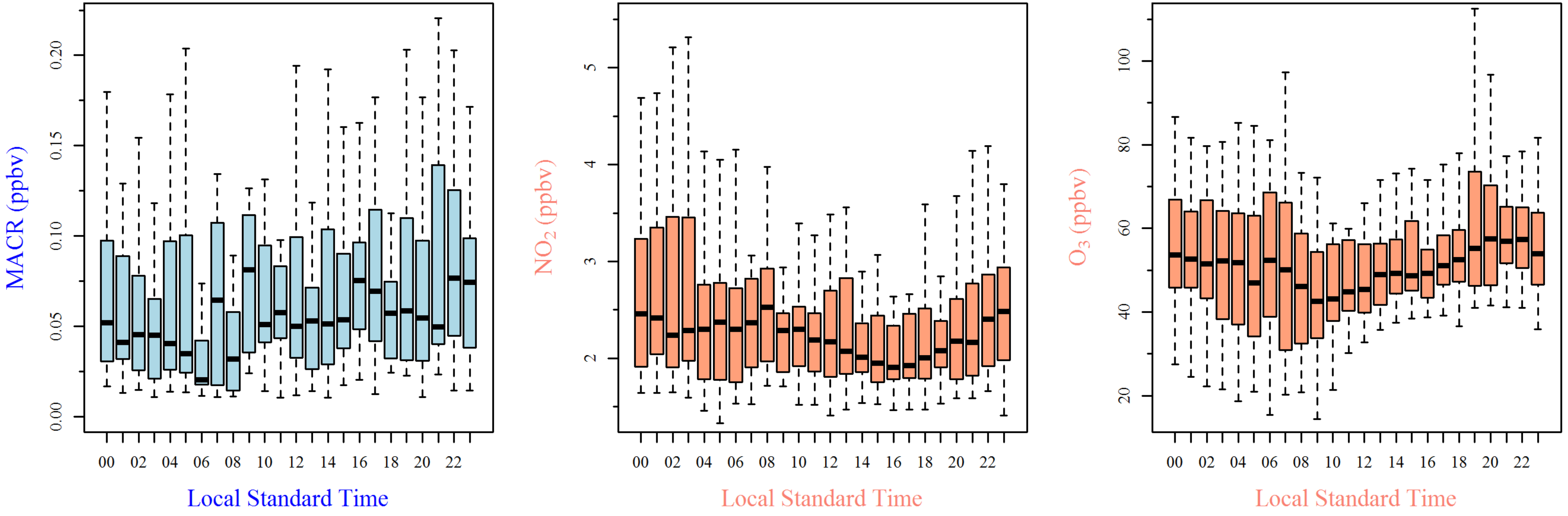
Temperature-dependent

Moderate correlation between daytime isoprene and temperature.



Diurnal variations

MACR were higher at night than daytime, consistent with NO_2 and O_3.

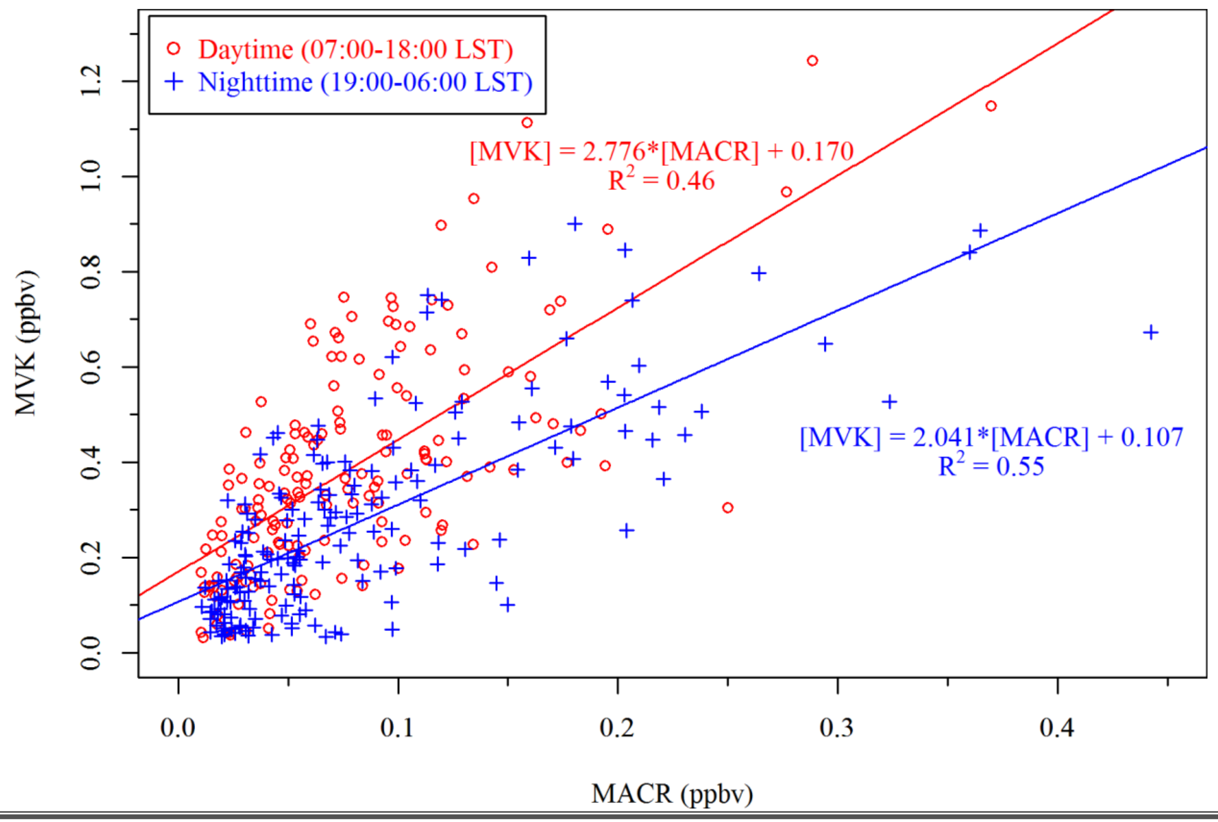


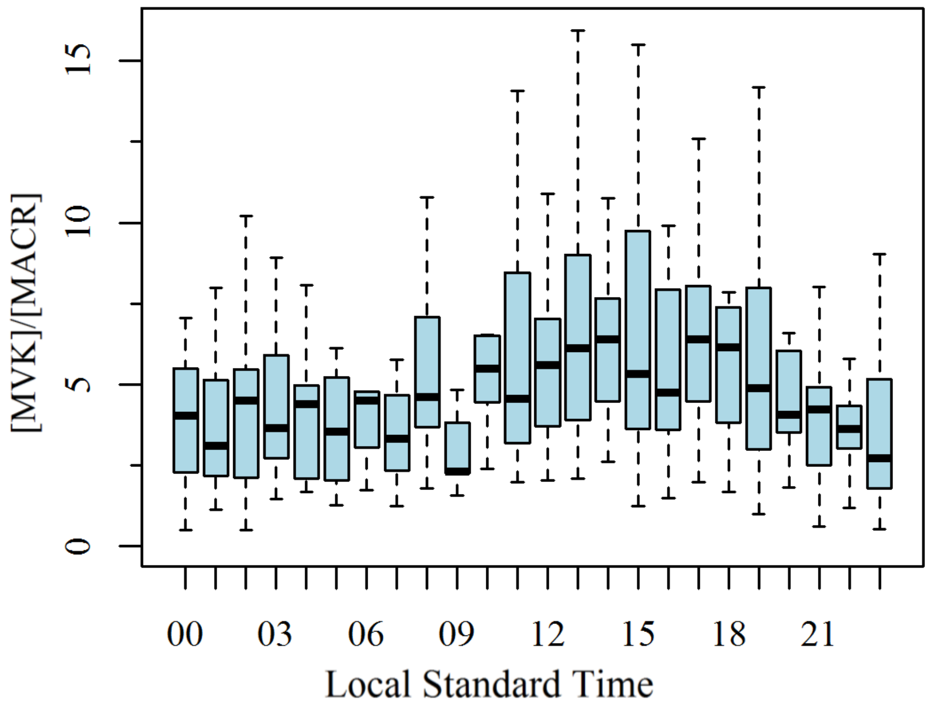
Correlations

Significant correlations between MVK and MACR: common source of isoprene oxidation.

Higher MVK/MACR ratios than the theoretical value (~2 in daytime and ~1 in nighttime):

OH- and NO_3-dominated oxidation in day- and night-time, respectively.

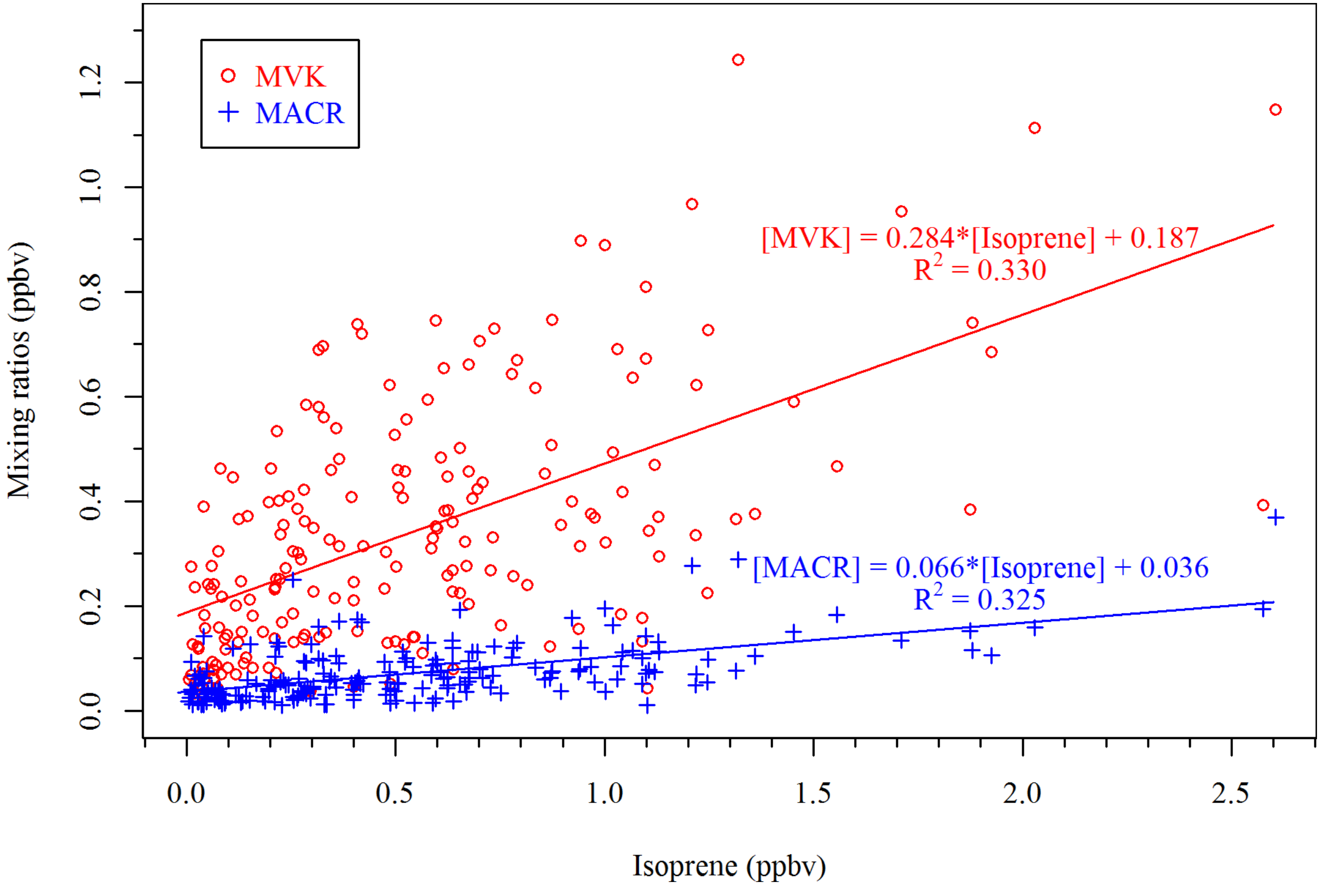




Correlations

Good correlations of isoprene with MACR and MVK:

"local" isoprene was probably responsible for the measured MVK and MACR.

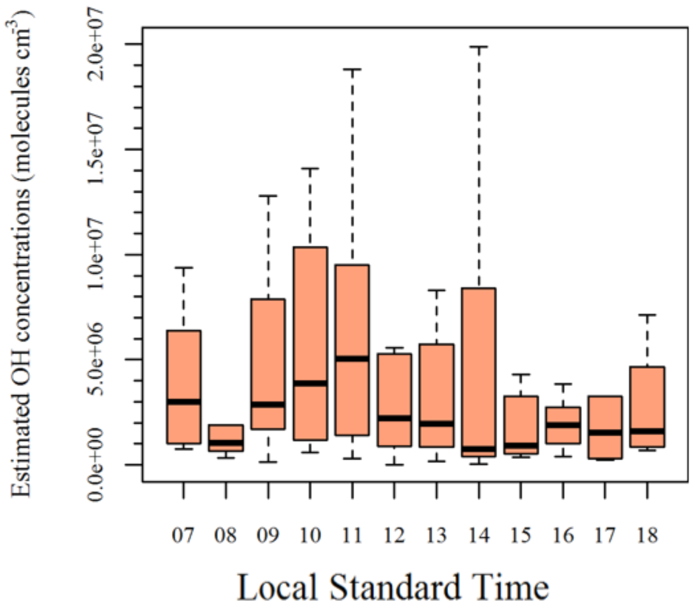


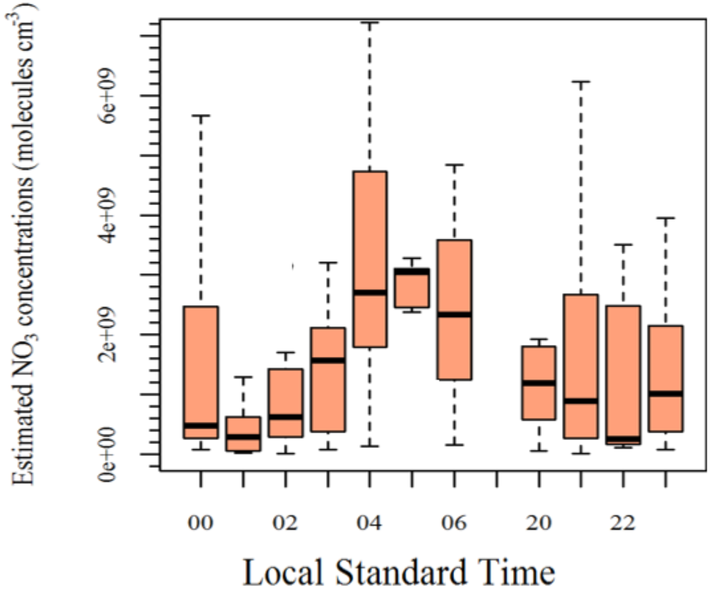
Rohrer et al., Nature Geosci., 2014.

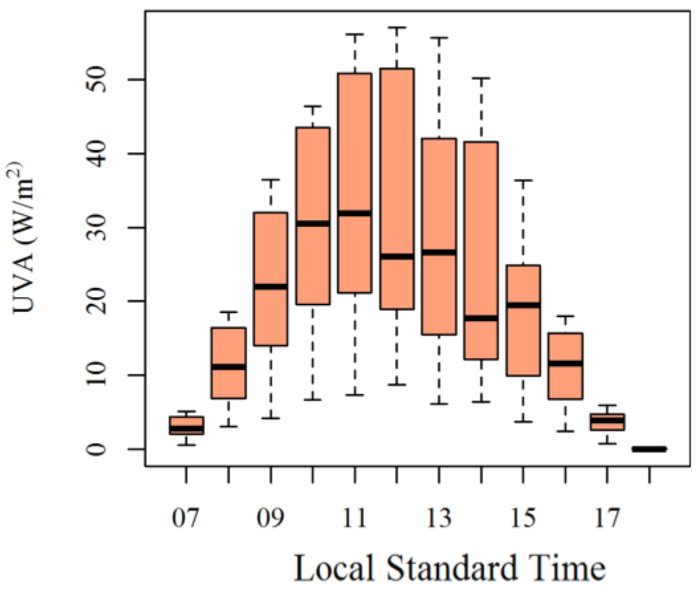
OH and NO_3 concentrations

Daytime OH concentrations: $5.1 \pm 1.4 \times 10^6$ molecules cm^{-3}, close to that observed by Xiao et al. (8.9×10^6 molecules cm^{-3}) at rural PRD; agrees well with solar radiation.

Nightime NO_3 levels: $10.4 \pm 2.2 \times 10^8$ molecules cm^{-3}, significantly higher than that simulated by Guo et al. at a mountain site in Hong Kong ($2.3 \pm 0.2 \times 10^8$ molecules cm^{-3}).



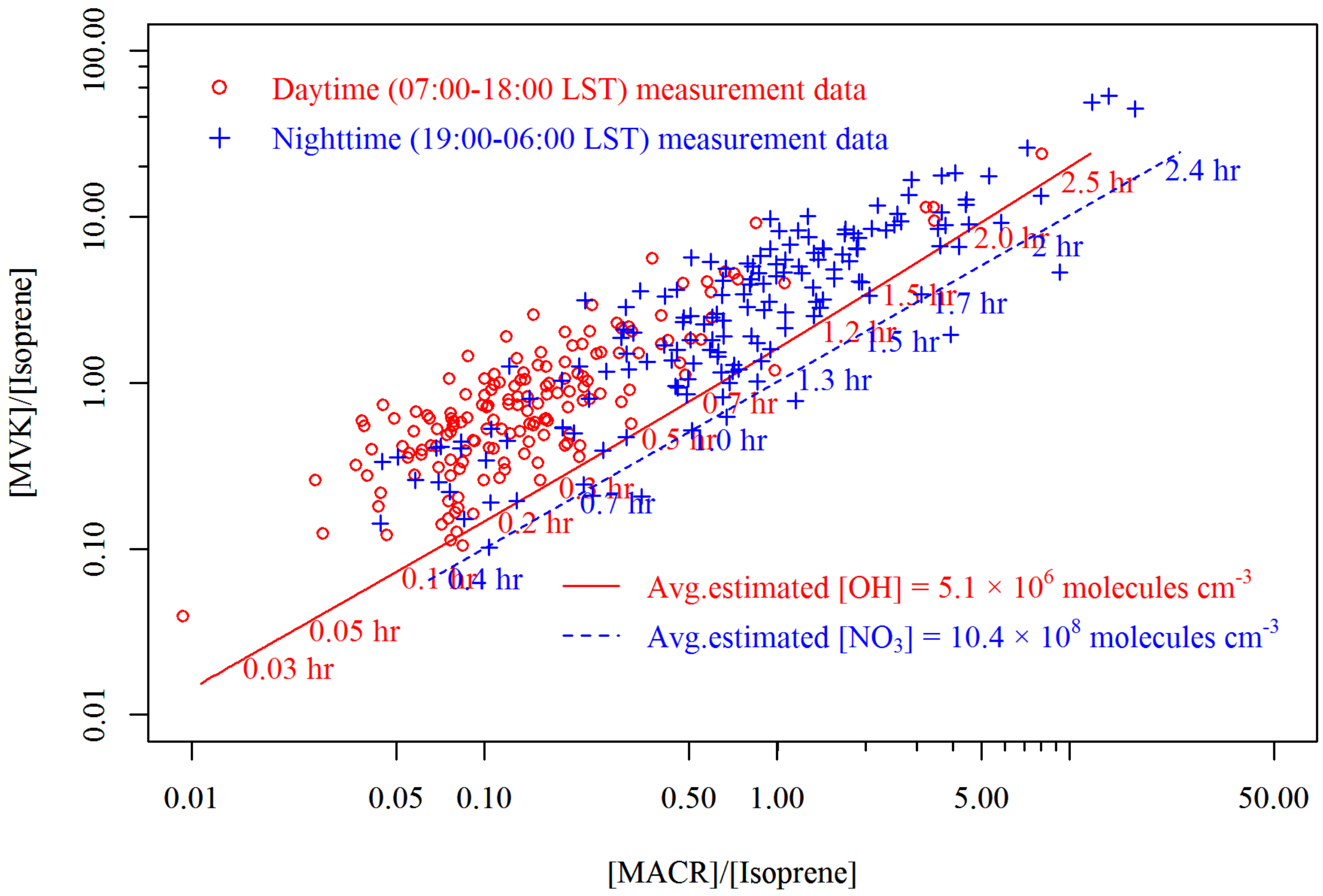




Atmospheric lifetime of isoprene

Daytime isoprene lifetime: 0.03~2.5 hour, with an average value around 0.3 hour.

Nighttime isoprene lifetime: 0.4~2.4 hour, mean value 1.3 hour.

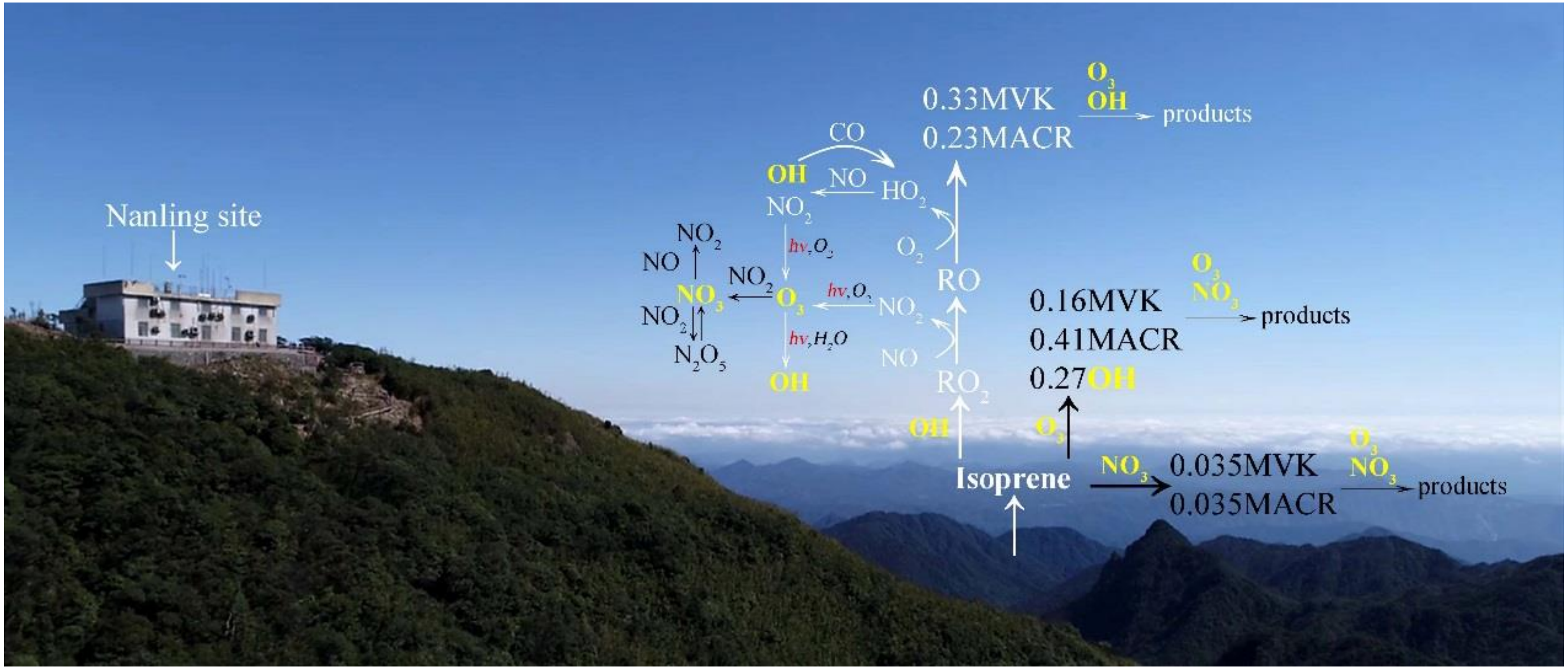


Ozone production

Total O_3 = O_x = $O_3 + NO_2$

This study, $[O_3 + NO_2] / [MVK]$=12.1 ppbv $ppbv^{-1}$.

41.3% of the O_3 production in daytime resulted from isoprene oxidation by OH in daytime.



Biesenthal et al., 1997.

Contents

1. Background
2. Methods
3. Results
4. Summary

Summary

1. Low isoprene and high [MVK+MACR]/Isoprene ratios were observed, most likely due to the high oxidative capacity.
2. High daytime and nightime MVK/MACR ratios were attributed to OH and NO_3 chemistry.
3. High daytime OH and nighttime NO_3 concentrations were estimated, implying the strong atmospheric oxidative capacity of this forested region.
4. The isoprene in daytime and nighttime periods were fast oxidized, with average chemical age of 0.3 hour and 1.3 hour, respectively.
5. Nearly 40% of the daytime O_3 production were resulted from OH reaction with isoprene.

Future work

1. High time resolution HCHO, OH and NO_3 measurements.
2. Vertical profiles within and above the convective boundary layer (CBL) obtaining.
3. More meteorological driving variables considering.
4. Chamber studies.

Acknowledgment

暨南大學 环境与气候研究院
JINAN UNIVERSITY INSTITUTE FOR ENVIRONMENTAL AND CLIMATE RESEARCH

http://ecins.jnu.edu.cn/

THANK YOU