BVOC emissions and O_3 in a subtropical plantation in China: measurement and validation

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1. Introduction

- Atmospheric pollution is a severe problem over large areas and cities in recent years in China, it is an important task to keep on our monitoring and satellite validation of trace gases, BVOC emissions, aerosols in China, especially at some representative sites.
- Our main activities are ground observations, validation of satellite retrievals and satellite data applications.
- To fulfill one of all above tasks, measurements of BVOC emissions, O_3 and solar radiation were carried out in a subtropical *Pinus* plantation in China during 2013-2016.
- Many BVOCs have a high reactivity with atmospheric lifetimes (minutes to hours or days) and play key roles in chemical and photochemical reactions in the atmosphere, i.e., the formation of O_3 and secondary organic aerosol (SOA).
- BVOCs play important connections between gases, liquids and particles through chemical and photochemical reactions, and participate in solar energy transfer through the atmosphere.
- It is an urgent task to accurately know the amount of BVOC emitted from typical ecosystems and their contributions to O_3 and SOA formation.

2. Measurements and methods

● BVOC (Biogenic Volatile Organic Compound) emission fluxes, O_3 concentration, solar radiation (global, direct, PAR) and meteorological Parameters (T, RH, E) were measured at Qianyanzhou subtropical Pinus plantation, Taihe county, Jiangxi province (26^{0}44’ N, 115^{0}40’ E, 110.8 m) from 22 May 2013 to 4 Jan. 2016.

Table 1 **BVOC emission flux sampling periods** from 22 May, 2013 to 4 January, 2016

Year	**Experimental periods**					
2013	A: 22 May-28 May	B: 29 June-6 July		C: 6 Aug.-13 Aug.		D: 7 Sep.- 11 Sep.
2014	E: 18 Jan.-19 Jan.	F: 23 July -27 July				
2015	G: 14 Jan. - 19 Jan.	H: 22 Apr. - 30 Apr.	I: 6 June -16 June	J: 23 Aug. - 4 Sep.	K: 2 - 7 Nov.	L: 31 Dec. 2015 - 4 Jan., 2016

Fig. 1 BVOCs, O_3 and Solar radiation measurement at Qianyanzhou

- **Air sample collections:**

  1) diurnal variation: 6:00, 9:00, 12:00, 15:00, 18:00.
  2) day – day variation: randomly, around noon

- **Sample analysis:**
  The sampled cartridges were stored in a refrigerator and analyzed by GC- FID and GC-MS

- **Flux calculation:**

a) REA technique

$$\mathbf{F = b\sigma_w(C_{up}-C_{down})} \qquad \mathbf{(1)}$$

b: a proportionality factor
$\boldsymbol{\sigma_w}$: standard deviation of the vertical wind speed
$\mathbf{C_{up}-C_{down}}$: concentration difference between the updraft and downdraft cartridges over a period of 30 min

b) Gradient method

$$\mathbf{F = K_{diff} \triangle C/\triangle Z} \qquad \mathbf{(2)}$$

K_{diff} : the eddy diffusion coefficient, K_{diff} =(k) (u*) (z-d) for neutral atmospheric stability, k=0.4 (von Karmons constant)

z : the measurement height

d : the displacement height

3. Results: a. BVOC emissions, diurnal and seasonal variations

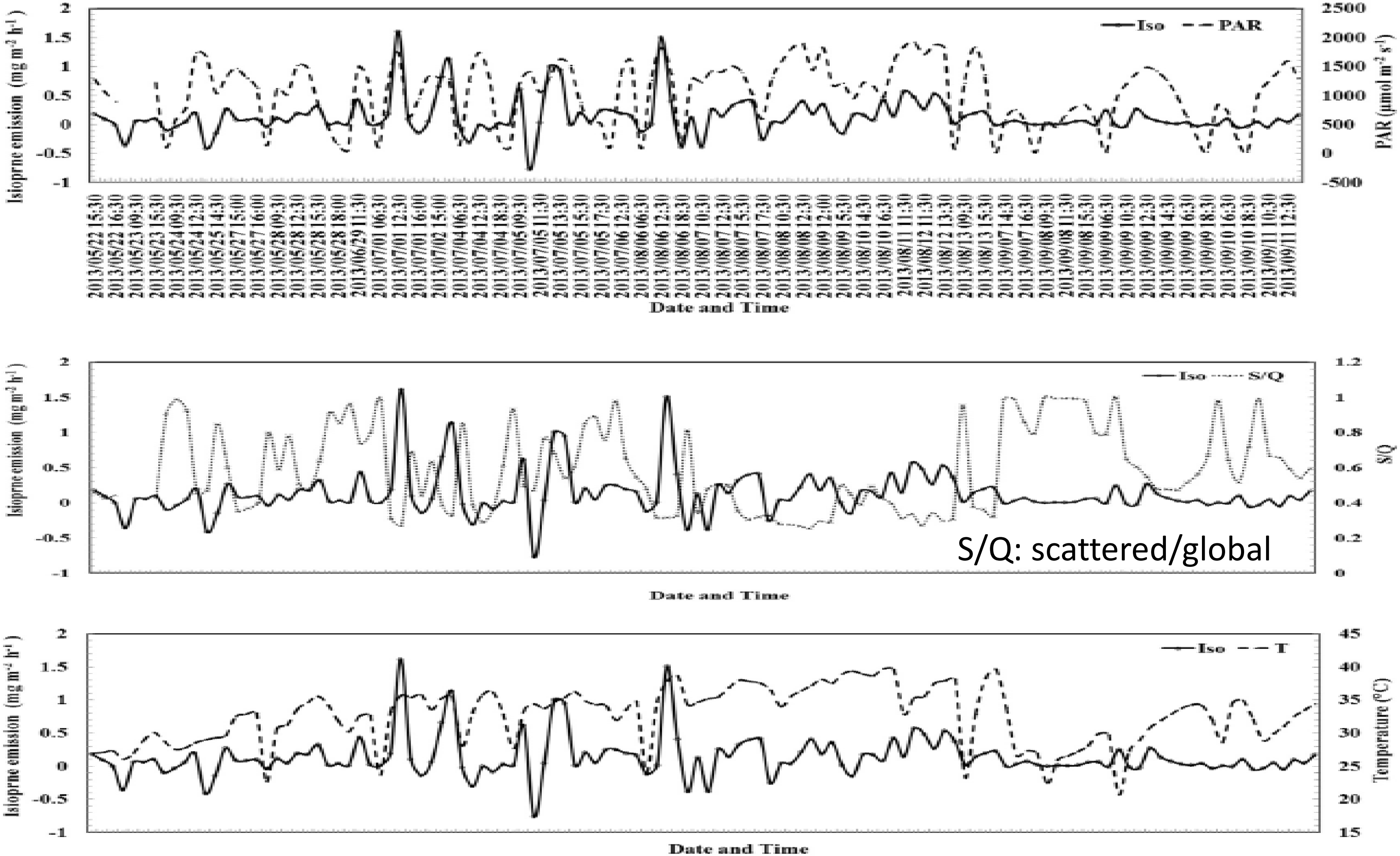


Fig. 2. Isoprene emission flux (Iso), PAR, S/Q and temperature (T) observed during 2013 (Bai et al., 2017)

Table 2 **Average and median of BVOC emission fluxes** (average, median, mg m^{-2} h^{-1}), normalized isoprene and monoterpene emission factors (Iso EF and MT EF) calculated by MEGAN and EMBE (mg m^{-2} h^{-1}), PAR (μmol m^{-2} s^{-1}), temperature (°C), S/Q, WV (water vapor, hPa) and O_3 concentrations (average, maximum, ppb) during different periods.

	A (22 May-28 May, 2013)	B (29 June-6 July, 2013)	C (6 Aug.-13 Aug., 2013)	D (7 Sep.-11 Sep., 2013)	E (18 Jan.-19 Jan., 2014)	F (23 July - 27 July, 2014)
Isoprene	0.042,0.056	0.237,0.079	0.203,0.177	0.044,0.025	0.087,0.000	0.259,0.302
α-pinene	0.248,0.275	0.434,0.482	0.432,0.382	0.190,0.193	0.188,0.044	0.389,0.354
Camphene	0.007,0.013	0.017,0.016	0.025,0.017	0.010,0.009	0.182,0.029	0.065,0.060
……						
Iso EF (MEGAN, EMBE)	0.163,1.012	0.466,0.369	0.184,-0.126	0.142,1.175	- ,1.190	0.404,1.058
MT EF (MEGAN, EMBE)	1.002,1.428	1.154,1.201	0.726,1.136	0.853,1.528	1.381,1.965	1.165,1.394
PAR	979.0	1043.9	1292.6	793.5	705.9	896.2
T	29.9	33.5	36.1	29.9	11.6	31.9
WV	31.2	29.9	28.3	31.5	6.8	36.2
S/Q	0.64	0.62	0.41	0.74	0.61	0.76
O_3 (avg,max)	34.4,64.4	43.6,75.6	41.1,63.4	42.8,59.3	51.4,71.6	49.0,110.9

- Isoprene: 21.2%; α-pinene, camphene, β-pinene and limonene: 51.5%, 2.4%, 9.1%, 13.0%
- Higher BVOC emissions: in summer (60%-84% in 2013), associated with higher PAR and T

b. Other factors affecting BVOC emissions: biomass burning smoke, florescence

Table 3 **BVOC emission fluxes** (mg m^{-2} h^{-1}), PAR (μmol m^{-2} s^{-1}), temperature (^oC), S/Q (scattering factor), WV (water vapor pressure at the ground, hPa) and O_3 concentrations (ppb) **during different sampling periods**.

	12:00-12:30, 23 July, 2014	12:00-12:30, 25 July, 2014	16:00-16:30, 2 Nov., 2015	17:00-17:30, 2 Nov., 2015	10:00-15:30, 22 Apr., 2015	10:00-16:30, 26 Apr., 2015
event	**smoke**	**no smoke**	**no smoke**	**smoke**	**florescence**	**no florescence**
isoprene	0.308	0.779	0.096	0	0	-0.154
monoterpenes	**1.704**	0.893	0.145	**0.472**	**0.693**	-0.169
PAR	1195.5	1499.2	194.4	47.9	1013.1	1376.3
T	36.5	33.2	15.7	13.5	20.8	26.1
WV	40.1	35.3	15.4	15.1	18.6	23.7
S/Q	0.76	0.61	0.79	0.98	0.79	0.62
O_3	**110.9**	60.6	49.8	**50.5**	44.3	52.0

* BVOC emissions increased

c. Comparison of BVOC emissions at typical ecosystems in China

Table 4 **Average (avg) and maximum (max) emission fluxes** (mg m^{-2} h^{-1}) of isoprene and monoterpenes measured at typical ecosystems

Ecosystem	**Isoprene**		**Monoterpenes**		**measuring period**	**References**
	avg	max	avg	Max		
Grassland	0.76				June-Sep., 2002; Sep., 2003	Bai et al.(2003)
tropical forest	1.0				July, 2002	Baker et al.(2005)
subtropical forest		0.215		0.313		Situ et al.(2013)
temperate forest	1.275	4.775	0.195	1.061	19 June to 30 June, 2010	Bai et al.(2015)
subtropical Lei bamboo forest	0.95	10.32	0.010	0.176	7 July, 2012 to 19 Jan., 2013	Bai et al.(2016)
subtropical Lei bamboo forest	**2.81**	10.32	0.011	0.121	7 July to 13 July, 2012	Bai et al.(2016)
subtropical pine plantation	0.137	1.610	**0.474**	2.711	22 May to 11, Sep., 2013	This study
subtropical pine plantation	-0.001	1.938	0.357	3.995	1 Jan., 2014 to 4 Jan., 2016	This study

- Subtropical forests are the highest BVOC emitters: bamboo-isoprene, pinus-monoterpenes.

d: Model simulation of BVOC emissions in a subtropical *pinus* plantation

- **Empirical model of BVOC emissions (EMBE)** (based on PAR energy balance) **:**

$$\mathbf{e^{-k1Etm} \times \cos Z = A_1 PAR \times \cos Z + A_2 e^{-kwm} \times \cos Z + A_3 e^{-S/Q} + A_0} \quad \textbf{(3)}$$

Terms: isoprene PAR photochemical scattering

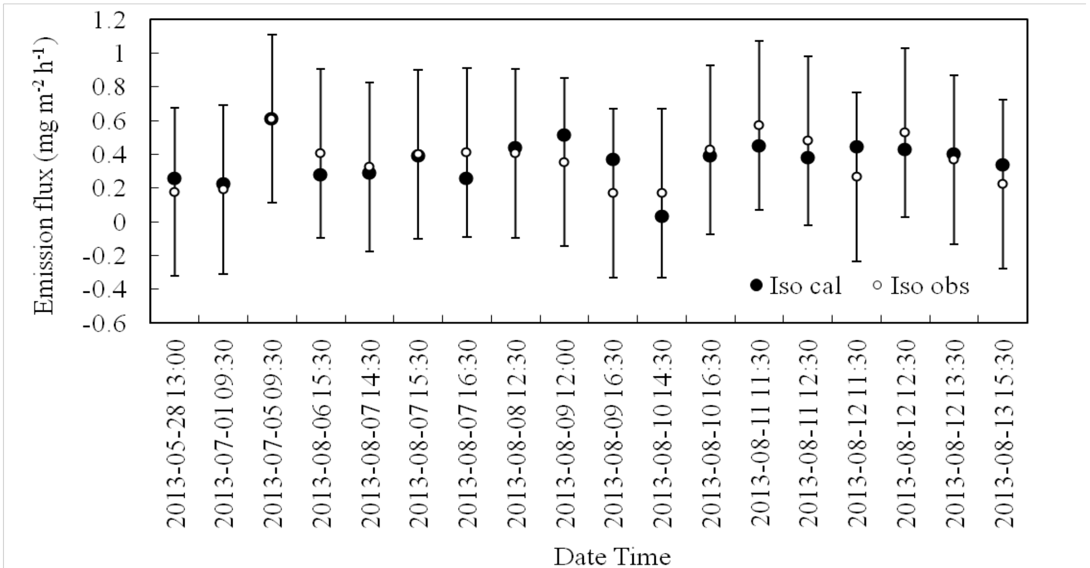


Fig. 3 The observed and calculated **isoprene emission fluxes** (Iso obs and Iso cal), the observed fluxes show error bars as one standard deviation

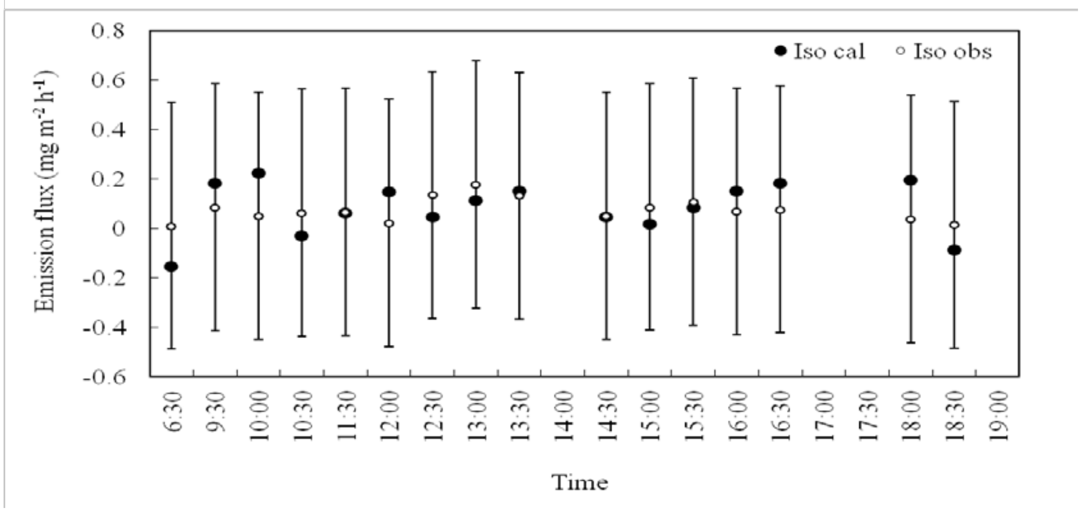


Fig. 4 Calculated and observed **average diurnal variation of isoprene emission** (n=61), emission fluxes within twice the standard deviation of average observed emissions

● **BVOC emissions from 2013 to 2016**

Isoprene emissions were calculated by EMBE and the observational emissions:

Input: solar radiation (PAR, S, Q) and meteorological data (T, E).

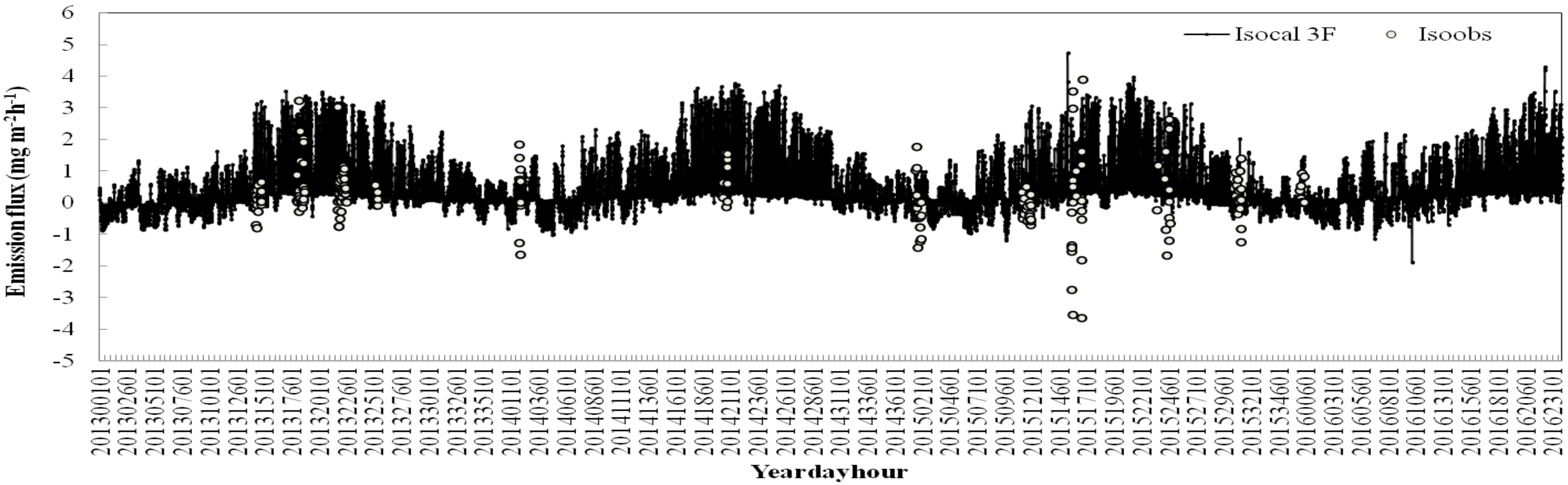


Fig. 5 Isoprene simulations using 3-Factor empirical model (Isocal 3F) and measured emissions (Isoobs) from January 1, 2013 to December 31, 2016

Year	Isoprene	MT	BVOCs
2013	1571.1	2721.6	5460.2
2014	3087.7	2702.8	5881.2
2015	2650.5	2475.7	5204.6
2016	2023.2	2603.6	4859.4

Total annual BVOC emissions (mg m^{-2}) during 2013- 2016 (Table 5)

● Isoprene, monoterpenes, BVOCs: decreased during last 4 years

e. Summary of emission model of BVOC emissions

Table 6 **The coefficients and constants of EMBE**, coefficient of determination (R^2), average of the absolute relative bias (δ,%), normalized mean square error (NMSE), and standard deviations of calculated and observed fluxes (σcal, σobs)
Qianyanzhou subtropical *pinus* plantation-**QYZ**, LinAn subtropical bamboo forest-**LA**
Changbai Mountain temperate forest-**CBS** **(For isoprene)**

Site	**A_1**	**A_2**	**A_3**	**A_0**	**R^2**	**δ**	**NMSE**	**σcal**	**σobs**
QYZ	-0.052	1.408	0.106	-0.036	0.999	32.8	0.092	0.124	0.135
LA	-0.050	1.331	0.298	-0.226	0.932	20.3	0.031	0.454	0.857
CBS	-0.049	1.292	0.112	-0.065	0.964	39.3	0.133	0.412	0.637

- **A_1 and A_1** represent the roles of PAR and photochemical terms, respectively
- **photochemical term:** PAR energy utilization by atmospheric gases, liquids and particles (GLPs), which was associated with water vapor and temperature
- A_1 and A_1 were similar for 3 typical forests in China, respectively

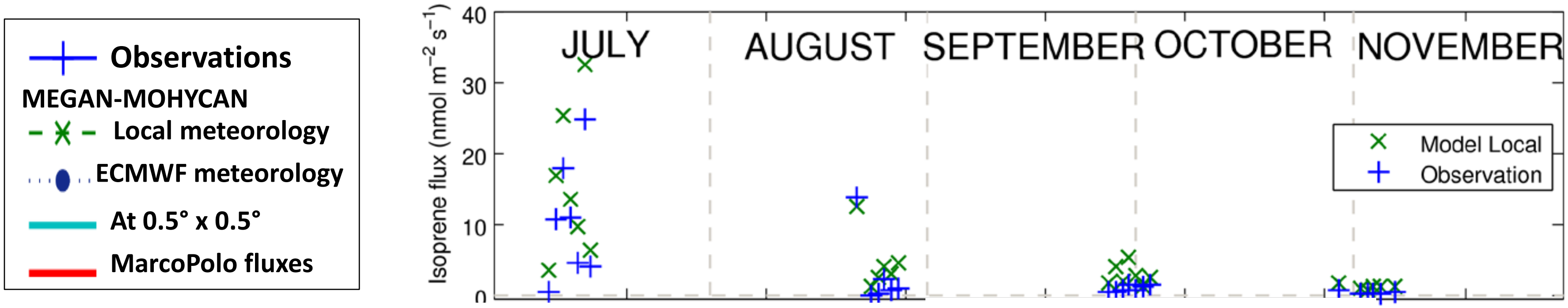
Table 7 **BVOC emission factors** (at standard conditions-T=30^{o}C, PAR=1500 μmol m^{-2} s^{-1}) at some ecosystems in China calculated by empirical (EMBE) and MEGAN models.

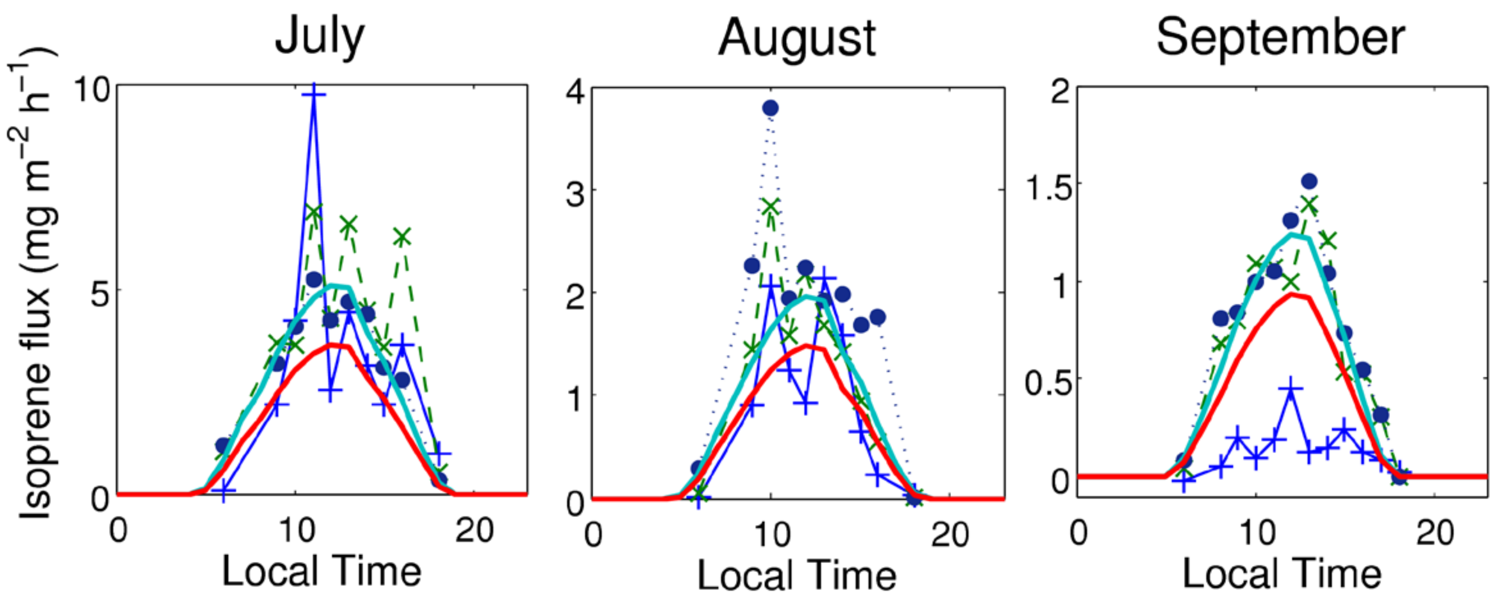
Ecosystems	**Emission factor** (mg m^{-2} h^{-1})			
	Empirical model		**MEGAN**	
	Isoprene	**Monoterpenes**	**Isoprene**	**Monoterpenes**
Inner Mongolia grassland	0.48		0.38-0.52	
Changbai Mountain temperate forest (CBS)	2.50	0.40	3.60	0.32
Subtropical bamboo forest (LinAn)	**4.00**	0.12	**3.60**	0.16
Subtropical pinus plantation (QYZ)	1.19	**1.65**	0.71	**1.19**

• Subtropical forests are the highest BVOC emitters: bamboo-isoprene, pinus-monoterpenes, **corresponding to the measurements**

* BVOC emission fluxes of Changbai temperate and subtropical bamboo forests can also be downloaded from VOCsNET: http://vocsnetdata.ceh.ac.uk/page/login.aspx

f. Model simulation





- **The space-based inventory provides a satisfactory agreement with the observations in July and August.**

July	Mean	r	August	Mean	r	September	Mean	r
Observations	3.30			0.98			0.14	
MEGAN-MOHYCAN Local	4.09	0.79		1.27	0.84		0.72	0.47
MEGAN-MOHYCAN ECMWF	3.30	0.74		1.79	0.76		0.77	0.62
At 0.5° x 0.5°	3.31	0.63		1.23	0.82		0.69	0.66
MarcoPolo Inventory	2.36	0.63		0.92	0.83		0.52	0.67

4. Summary

- Isoprene and monoterpene emissions were the highest in summer, contributing more than half of the total annual emission.
- Monoterpenes were the dominant BVOCs in this subtropical *Pinus* plantation.
- Annual BVOC emissions decreased in 2015 compared with 2013, which were associated with decreases of PAR, temperature and water vapor.
- BVOC emissions were influenced by biomass burning smoke and pine florescence.
- An empirical model of BVOC emissions was developed.
- Isoprene, monoterpene and BVOCs emissions decreased during last 4 years.
- The mean emission factors using the MEGAN and empirical model of BVOC emissions were 0.71 and 1.19 mg m^{-2} h^{-1} for isoprene and 1.39 and 1.65 mg m^{-2} h^{-1} for monoterpenes, respectively.
- The space-based inventory provides a satisfactory agreement with the isoprene emission in summer.

Thank you for your attention!