Supplement of Atmos. Chem. Phys. Discuss., 15, 31621–31663, 2015
http://www.atmos-chem-phys-discuss.net/15/31621/2015/
doi:10.5194/acpd-15-31621-2015-supplement

Atmospheric Chemistry and Physics Discussions

Supplement of

Understanding isoprene photo-oxidation using observations and modelling over a subtropical forest in the Southeast US

L. Su et al.

Correspondence to: J. E. Mak (john.mak@stonybrook.edu)

1 Algorithms used in ToFIND

1.1 Peak shape fitting

The peak generated by the PTR-TOF-MS is asymmetric and can be mathematically approximated by peak-shaped functions. Here we choose an empirically transformed Gaussian function (ETG) model to describe a single peak produced by the instrument (Li, 1997). The ETG is based on the decomposition of Gaussian function into leading and trailing edge functions. The two functions are weakly combined and subsequently modified, making it very suitable for approximating asymmetric peak shapes. The ETG is given by:

$$f(t) = \frac{H}{\{1+\lambda_L \exp[k_L(t_L - t)]\}^{\alpha} + \{1+\lambda_T \exp[k_T(t - t_T)]\}^{\beta} - 1} \quad \text{(S1)}$$

where f(t) denotes peak function; t denotes time-of-flight; H is related to peak height; λ_L and λ_T are pre-exponential parameters; k_L and k_T are the parameters related to the speeds of the rise and fall of the leading and trailing edges, respectively; t_L and t_T are the inflection times of the leading and trailing edges, respectively, and are fixed values; α and β are the parameters to further modify the shapes of the lading and trailing edges, respectively. The ETG features in a weak link between the leading and trailing parts of a single peak, thus is very flexible and suitable for fitting asymmetric peaks. The values of t_L and t_T do not need to be accurate, here we use the time-of-flight at the full width at half maximum (FWHM) on the left and right side of a single peak to represent those two values, respectively. There are a total of seven parameters in each ETG (H, λ_L, λ_T, k_L, k_T, α, and β), and the rate of convergence is fast. Levenberg-Marquardt algorithm is used to solve the non-linear least-squares curve fitting problem. To achieve a sufficiently high speed of the curve fitting, MINPACK-1 Least Squares Fitting Library in C (http://www.physics.wisc.edu/~craigm/idl/cmpfit.html) is used and integrated into the ToFIND toolbox through MATLAB-C interface (http://www.imm.dtu.dk/~guuru/).

1.2 Time-of-flight to m/z conversion

In the field free area of the TOF-MS, the time-of-flight of ions show slow drift due to the change in the length of the ions' flight path caused by temperature variations in this area. To

gain a high mass accuracy, continuous mass scale correction is performed on the raw data. Four well identified peaks: three internal ions (H218OH+, m/z=21.022, NO+, m/z=29.997, and H216OH218OH+, m/z=39.033), and one externally added compound (diiodomethane, fragmented at ion CH2I+, m/z=140.920) are used for mass scale correction peaks. The time-of-flight t and mass scale m/z are related to each other through:

$$t = a\sqrt{m/z} + b \quad \text{(S2)}$$

For each raw HDF5 data file, every 3 of the 300 spectra are averaged to produce 100 spectra. For each of the 100 spectra, the peak shape fitting algorithm described above is applied to find the peak centers (t) of the four mass scale correction peaks. Since the exact m/z values for each peak are known, the values of a and b in Eqn. A2 are calculated through linear least-squares method. The relative mass error (RME) is less than 10 parts per million (ppm) over the spectrum after mass scale calibration.

1.3 Peak detection

After time-of-flight to m/z conversion, the 300 mass scale corrected spectra are aligned with each other, and averaged to produce one single spectrum. A target mass list is predefined which includes a series exact m/z of interested VOCs compounds (e.g., methanol, acetone, isoprene, MVK+MACR, and monoterpenes). For one specific target peak, there may be other peaks co-existing in the same nominal m/z, a peak searching routine is used to find all the peaks including the target peak within a certain range of one nominal m/z. The mass list is then updated and used for peak shape fitting (see next section).

1.4 Signal integration

A few issues exist when performing signal integration on each individual peak: (1), due to the low counts rate in each individual 1 Hz spectrum, the peak shape fitting algorithm often fails to converge or generate desirable fitting results when applied to a single spectrum, (2), interference exists between two neighbouring peaks when they overlap with each other due to the limited mass resolution of the PTR-TOF-MS. To improve the accuracy of the peak fitting result, the updated peak list is used and the peak shape fitting algorithm is applied to the averaged spectrum described above to produce a peak function. Based on this, the FWHM for each peak is recalculated and used to define the peak integration boundaries. For the asymmetrical Gaussian-shaped peak which is typical for the PTR-TOF-MS, the integration

boundaries on the left and right sides are processed separately. With the updated FWHM values for all the peaks, the ratios of the portion before the peak center to the portion after the peak center are calculated and averaged (r). The integration boundary on the left side is defined as a*FWHM*r to the left of the peak center. The integration boundary on the right side is defined as a*FWHM*(1-r) to the right of the peak center. Add a figure to describe the procedure. The factor a is set to 4 for single peak and 3 for multiple peaks. The factor value is reduced for multiple peaks to lower the interference of neighbouring peaks.

Table S1. Other observations during the 2013 SAS campaign used in this study. Days used are during June 5, 6, 8, 10-13 unless otherwise specified in the table.

Parameter	Platform	Instrument/technique	Uncertainty	Days used	Institute
VOC	Airborne (NCAR C-130)	Proton Transfer Reaction Mass Spectrometer (PTR-MS)	20%	June 12	NCAR, NOAA
ISOPN	SEARCH site	chemical ionization mass spectrometer (CIMS)	25%	June 5, 6, 8, 10-13	Purdue University
O3, NOx	Airborne (NCAR C-130)	chemiluminescence	10% for NO, 15% for NO2, 5% for O3	June 12	NCAR
O3, NOx	SEARCH tower	ThermoScientific 49i, 42i	5.5% for NO, 15.0% for NO2, 6.1% for O3	June 5, 6, 8, 10-13	ARA
OH	SEARCH tower	laser induced fluorescence (LIF)	32%	June 5, 6, 8, 10-13	Pennsylvania State University
Surface heat flux	AABC tower	Integrated Surface Flux System (ISFS)		June 10-13	NCAR
Potential temperature specific humidity	AABC tower	ISFS		June 10-13	NCAR
Potential temperature specific humidity	Airborne (NCAR C-130)	onboard sensor		June 12	NCAR
Photolysis rates	Airborne (NCAR C-130)	onboard sensor		June 12	NCAR
Boundary layer height	SEARCH	Ceilometer, Integrated Sounding System (ISS)	13.0% for ceilometer	June 10-13	ARA, NCAR

Table S2. Chemical species in the complex scheme. See more details at http:// http://wiki.seas.harvard.edu/geos-chem/index.php/New_isoprene_scheme

Species	Formula	Note
A3O2	CH3CH2CH2OO	primary RO2 from C3H8
ACET	CH3C(O)CH3	acetone
ACTA	CH3C(O)OH	acetic acid
ALD2	CH3CHO	acetaldehyde
ALK4	RH	≥C4 alkanes
ATO2	CH3C(O)CH2O2	RO2 from acetone
ATOOH	CH3C(O)CH2OOH	ATO2 peroxide
B3O2	CH3CH(OO)CH3	secondary RO2 from C3H8
C2H6	C2H6	ethane
C3H8	C3H8	propane
CH2O	CH2O	formaldehyde
CH4	CH4	methane
CO	CO	carbon monoxide
CO2	CO2	carbon dioxide
DHMOB	HOCH2C(CH3)(OH)C(=O)CHO	See Paulot et al., ACP (2009)
DIBOO		Dibble peroxy radical
EOH	C2H5OH	ethanol
ETHLN	CHOCH2ONO2	Ethanal nitrate
ETO2	CH3CH2OO	ethylperoxy radical
ETP	CH3CH2OOH	ethylhydroperoxide
GLYC	HOCH2CHO	glycoaldehyde (hydroxyacetaldehyde)
GLYX	CHOCHO	glyoxal
H2	H2	hydrogen atom
H2O	H2O	water vapor
H2O2	H2O2	hydrogen peroxide
HAC	HOCH2C(O)CH3	hydroxyacetone
HCOOH	HCOOH	formic acid
HC5	HOCH2CH=C(CH3)CHO	Hydroxycarbonyl with 5C
HC5OO		Peroxy radical from HC5 (old IAO2?)
HNO2	HONO	nitrous acid
HNO3	HNO3	nitric acid
HNO4	HNO4	pernitric acid
HO2	HO2	hydroperoxyl radical
IALD	HOCH2C(CH3)=CHCHO	hydroxy carbonyl alkenes from isoprene
IAP	HOCH2C(CH3)(OOH)CH(OH)CHO	peroxide from IAO2
IEPOX		Isoprene epoxide
IEPOXOO		RO2 from IEPOX
INO2	O2NOCH2C(OO)(CH3)CH=CH2	RO2 from ISOP+NO3
INPN	O2NOCH2C(OOH)(CH3)CH=CH2	peroxide from INO2
ISN1		nighttime isoprene nitrate

ISNOOA		peroxy radical from ISN1
ISNOOB		peroxy radical from ISN1
ISNOHOO		peroxy radical from ISN1
ISNP	HOCH2C(OOH)(CH3)CH(ONO2)CH2OH	peroxide from ISOPNBO2 and ISOPNDO2
ISOP	CH2=C(CH3)CH=CH2	isoprene
ISOPNB	C5H9NO4	Isoprene nitrate Beta
ISOPND	C5H9NO4	Isoprene nitrate Delta
KO2	RO2 from >3 ketones	RO2 from >3 ketones
M		for three body reactions
MACR	CH2=C(CH3)CHO	methacrolein
MACRN	HOCH2C(ONO2)(CH3)CHO	Nitrate from MVK
MAN2	HOCH2C(ONO2)(CH3)CHO	RO2 from MACR+NO3
MAO3	CH2=C(CH3)C(O)OO	peroxyacyl from MVK and MACR
MAOP	CH2=C(CH3)C(O)OOH	peroxide from MAO3
MAOPO2	CH2OH-CHOO*CH3C(O)OOH	Peroxy radical from MAOP (addition on the double bond)
MAP	CH3C(O)OOH	peroxyacetic acid
MCO3	CH3C(O)OO	peroxyacetyl radical
MEK	RC(O)R	>3 ketones
MGLY	CH3COCHO	methylglyoxyal
MNO3	CH3ONO2	methylnitrate
MOBA	HOC(=O)C(CH3)=CHCHO	5C acid from isoprene
MOBAOO		RO2 from MOBA
MO2	CH3O2	methylperoxy radical
MOH	CH3OH	methanol
MP	CH3OOH	methylhydroperoxide
MRO2	HOCH2C(OO)(CH3)CHO	RO2 from MACR+OH
MRP	HOCH2C(OOH)(CH3)CHO	peroxide from MRO2
MVK	CH2=CHC(=O)CH3	methylvinylketone
MVKN	HOCH2CH(ONO2)C(=O)CH3	Nitrate from MACR
N2	N2	nitrogen
N2O	N2O	nitrous oxide
N2O5	N2O5	dinitrogen pentoxide
NH2	NH2	ammonia radical
NH3	NH3	ammonia
NO	NO	nitric oxide
NO2	NO2	nitrogen dioxide
NO3	NO3	nitrate radical
O2	O2	molecular oxygen
O2CH2OH	O2CH2OH	produced by CH2O+HO2
O3	O3	ozone
OH	OH	hydroxyl radical
PAN	CH3C(O)OONO2	peroxyacetylnitrate
PMN	CH2=C(CH3)C(O)OONO2	peroxymethacryloyl nitrate (MPAN)
PO2	HOCH2CH(OO)CH3	RO2 from isoprene
PP	HOCH2CH(OOH)CH3	peroxide from PO2

PPN	CH3CH2C(O)OONO2	peroxypropionylnitrate
PRN1	O2NOCH2CH(OO)CH3	RO2 from propene + NO3
PRPE	C3H6	≥C4 alkenes
PRPN	O2NOCH2CH(OOH)CH3	peroxide from PRN1
PROPNN	CH3C(=O)CH2ONO2	Propanone nitrate
PYAC	CH3COCOOH	Pyruvic acid
R4N1	RO2 from R4N2	RO2 from R4N2
R4N2	RO2NO	≥C4 alkylnitrates
R4O2	RO2 from ALK4	RO2 from ALK4
R4P	CH3CH2CH2CH2OOH	peroxide from R4O2
RA3P	CH3CH2CH2OOH	peroxide from A3O2
RB3P	CH3CH(OOH)CH3	peroxide from B3O2
RCHO	CH3CH2CHO	>C2 aldehydes
RCO3	CH3CH2C(O)OO	peroxypropionyl radical
RCOOH	C2H5C(O)OH	>C2 organic acids
RIO1	HOCH2C(OO)(CH3)CH=CHOH	RO2 from isoprene oxidation products
RIO2	HOCH2C(OO)(CH3)CH=CH2	RO2 from isoprene (named as ISOPO2 in the literature)
RIP	HOCH2C(OOH)(CH3)CH=CH2	peroxide from RIO2 (named as ISOPOOH in the literature)
ROH	C3H7OH	>C2 alcohols
RP	CH3CH2C(O)OOH	peroxide from RCO3
VRO2	HOCH2CH(OO)C(O)CH3	RO2 from MVK+OH
VRP	HOCH2CH(OOH)C(O)CH3	peroxide from VRO2

1

2 Table S3. The complex chemical scheme used in MXLCH.

Reaction	Reaction rate
O + O2 + M -> O3 + M	6E-34*(300/T)^2.4
O + O3 -> 2O2	8.00E-12*exp(-2060/T)
O1D + N2 -> O + N2	2.10E-11*exp(115/T)
O1D + O2 -> O + O2	3.20E-11*exp(70/T)
O1D + H2O -> 2OH	2.20E-10
H2 + O1D -> HO2 + OH	1.10E-10
H2 + OH -> H2O + HO2	5.50E-12*exp(-2000/T)
O + OH -> HO2 + O2	2.20E-11*exp(120/T)
HO2 + O -> OH + O2	3.00E-11*exp(200/T)
OH + O3 -> HO2 + O2	1.70E-12*exp(-940/T)
HO2 + O3 -> OH + 2O2	1.00E-14*exp(-490/T)
2HO2 -> H2O2 + O2	(2.3E-13*exp(600/T)+1.7E-33*[M]*exp(1000/T))*(1 + 1.4E-21*[H2O]*exp(2200/T))
H2O2 + OH -> H2O + HO2	2.90E-12*exp(-160/T)
OH + HO2 -> H2O + O2	4.80E-11*exp(250/T)
2OH -> H2O + O	4.20E-12*exp(-240/T)
2OH -> H2O2	6.29E-12
N2O + O1D -> N2 + O2	4.90E-11
N2O + O1D -> 2NO	6.70E-11
NO + HO2 -> NO2 + OH	3.50E-12*exp(250/T)
NO + O3 -> NO2 + O2	3.00E-12*exp(-1500.0/T)
NO2 + O -> NO + O2	5.60E-12*exp(180/T)
NO2 + O3 -> NO3 + O2	1.20E-13*exp(-2450/T)
NO3 + HO2 -> OH + NO2	2.30E-12*exp(170/T)
NO2 + NO3 -> N2O5	1.16E-12
N2O5 -> NO2 + NO3	4.70E-02
NO2 + OH -> HNO3	3.50E-12*exp(340/T)
HNO3 + OH -> NO3	1.59E-13
NO3 + NO -> 2NO2	1.50E-11*exp(170/T)
NO2 + HO2 -> HO2NO2	1.37E-12
HO2NO2 + OH -> H2O + NO2 + O2	1.30E-12*exp(380/T)
HO2NO2 -> HO2 + NO2	8.50E-02
CH4 + OH -> MO2 + H2O	2.45E-12*exp(-1775/T)
CH4 + O1D -> .75MO2 + .75OH + .25CH2O + .4HO2 + .05H2	1.50E-10
MO2 + NO -> CH2O + NO2 + HO2	2.80E-12*exp(300/T)
2MO2 -> 2CH2O + 2HO2	5.00E-13*exp(-424/T)
2MO2 -> CH2O + MOH	1.90E-14*exp(706/T)
MO2 + HO2 -> MP + O2	4.10E-13*exp(750/T)
MP + OH -> .7MO2 + .3OH + .3CH2O + H2O	3.80E-12*exp(200/T)
CH2O + OH -> CO + H2O + HO2	9.00E-12
CO + OH -> (CO2) + HO2	2.40E-13

MOH + OH -> HO2 + CH2O	7.30E-12*exp(-620/T)
ISOP + OH -> RIO2	3.1E-11*exp(350/T)
MACR + OH -> 0.53MAO3 + 0.47MRO2	8.0E-12*exp(380/T)
MVK + OH -> VRO2	2.6E-12*exp(610/T)
PMN + OH -> HAC + CO + NO2	2.90E-11
GLYC + OH -> 0.732CH2O + (0.361CO2) + 0.505CO + 0.227OH + 0.773HO2 + 0.134GLYX + 0.134HCOOH	6.54E-12
GLYC + OH -> HCOOH + OH + CO	1.45E-12
GLYX + OH -> HO2 + 2CO	3.1E-12*exp(340/T)
HAC + OH -> MGLY + HO2	1.81E-12*exp(305/T)
HAC + OH -> 0.5HCOOH + OH + 0.5ACTA + (0.5CO2) + 0.5CO + 0.5MO2	3.43E-13*exp(305/T)
PRPN + OH -> 0.209PRN1 + 0.791OH + 0.791PROPNN	8.78E-12*exp(200/T)
ETP + OH -> 0.64OH + 0.36ETO2 + 0.60ALD2	5.18E-12*exp(200/T)
RA3P + OH -> 0.64OH + 0.36A3O2 + 0.64RCHO	5.18E-12*exp(200/T)
RB3P + OH -> 0.791OH + 0.209B3O2 + 0.791ACET	8.78E-12*exp(200/T)
R4P + OH -> 0.791OH + 0.209R4O2 + 0.791RCHO	8.78E-12*exp(200/T)
RP + OH -> RCO3	6.13E-13*exp(200/T)
PP + OH -> 0.791OH + 0.209PO2 + 0.791HAC	8.78E-12*exp(200/T)
RIP + OH -> 0.387RIO2 + 0.613OH + 0.613HC5	4.75E-12*exp(200/T)
RIP + OH -> OH + IEPOX	1.9E-11*exp(390/T)
IEPOX + OH -> IEPOXOO	5.78E-11*exp(-400/T)
IAP + OH -> 0.654OH + 0.654DHMOB + 0.346HC5OO	5.31E-12*exp(200/T)
VRP + OH -> 0.791OH + 0.791MEK + 0.209VRO2	8.78E-12*exp(200/T)
MRP + OH -> MRO2	1.84E-12*exp(200/T)
MRP + OH -> (CO2) + HAC + OH	4.40E-12*exp(380/T)
MAOP + OH -> MAO3	6.13E-13*exp(200/T)
MAOP + OH -> MAOPO2	3.60E-12*exp(380/T)
OH + MAP -> 1.0MCO3	6.13E-13*exp(200/T)
HC5 + OH -> HC5OO	3.35E-11*exp(380/T)
ISOPND + OH -> ISOPNDO2	2.64E-11*exp(380/T)
ISOPNB + OH -> ISOPNBO2	3.61E-12*exp(380/T)
ISNP + OH -> 0.612OH + 0.612R4N1 + 0.193ISOPNBO2 + 0.193ISOPNDO2	4.75E-12*exp(200/T)
MVKN + OH -> 0.650HCOOH + NO3 + 0.650MGLY + 0.350CH2O + 0.350PYAC	1.5E-12*exp(380/T)
MACRN + OH -> 1.0MACRNO2	1.39E-11*exp(380/T)
DHMOB + OH -> 1.5CO + 1.0HO2 + 0.5HAC + 0.5MEK	2.52E-11*exp(410/T)
MOBA + OH -> MOBAOO	2.79E-11*exp(380/T)
ETHLN + OH -> CH2O + (CO2) + NO2	1.00E-11
PROPNN + OH -> NO2 + MGLY	1.00E-15
ATOOH + OH -> ATO2 + H2O	2.66E-12*exp(200/T)
ATOOH + OH -> MGLY + OH + H2O	1.14E-12*exp(200/T)
R4N2 + OH -> R4N1 + H2O	1.60E-12
RIO2 + NO -> 0.883NO2 + 0.783HO2 + 0.660CH2O + 0.400MVK + 0.260MACR + 0.070ISOPND + 0.047ISOPNB + 0.123HC5 + 0.1DIBOO	2.70E-12*exp(350/T)
VRO2 + NO -> 0.88NO2 + 0.35HO2 + 0.35CH2O + 0.53MCO3 + 0.53GLYC + 0.35MGLY + 0.12MVKN	2.70E-12*exp(350/T)

MRO2 + NO -> 0.85NO2 + 0.85HO2 + 0.122MGLY + 0.728HAC + 0.728CO + 0.122CH2O + 0.15MACRN	2.70E-12*exp(350/T)
MAN2 + NO -> 1.5NO2 + 0.5CH2O + 0.5MGLY + 0.5PROPNN + 0.5CO + 0.5OH	2.70E-12*exp(350/T)
IEPOXOO + NO -> 0.725HAC + 0.275GLYC + 0.275GLYX + 0.275MGLY + 0.125OH + 0.825HO2 + (0.200CO2) + 0.375CH2O + 0.074HCOOH + 0.251CO + NO2	2.70E-12*exp(350/T)
MAOPO2 + NO -> 1.0HAC + (1.0CO2) + 1.0OH + 1.0NO2	2.48E-12
MAOPO2 + NO -> 1.0HNO3	2.24E-13
HC5OO + NO -> NO2 + 0.216GLYX + 0.234MGLY + 0.234GLYC + 0.216HAC + 0.290DHMOB + 0.170MOBA + 0.090RCHO + HO2 + 0.090CO	2.48E-12
HC5OO + NO -> HNO3	3.42E-13
ISOPNDO2 + NO -> 0.070MACRN + 0.310HCOOH + 0.440HAC + 0.130ETHLN + 0.650CH2O + 1.34NO2 + 0.150GLYC + 0.310NO3 + 0.150PROPNN + 0.340MEK + 0.350HO2	2.48E-12
ISOPNDO2 + NO -> HNO3	3.42E-13
ISOPNBO2 + NO -> 0.6GLYC + 0.6HAC + 0.4CH2O + 1.6NO2 + 0.26MACRN + 0.4HO2 + 0.14MVKN	2.48E-12
ISOPNBO2 + NO -> HNO3	3.42E-13
MACRNO2 + NO -> 0.08ACTA + 0.08CH2O + 0.15NO3 + 0.07HCOOH + 0.070MGLY + 0.850HAC + 0.85NO2 + (0.93CO2) + 1.0NO2	2.7E-12*exp(350/T)
DIBOO + NO -> HO2 + NO2 + 0.520GLYC + 0.520MGLY + 0.480HAC + 0.480GLYX	2.48E-12
DIBOO + NO -> HNO3	3.42E-13
MOBAOO + NO -> RCHO + (CO2) + HO2 + NO2	2.48E-12
MOBAOO + NO -> HNO3	3.42E-13
MAN2 + NO -> 1.5NO2 + 0.5CH2O + 0.5MGLY + 0.5PROPNN + 0.5CO + 0.5OH	2.70E-12*exp(350/T)
MCO3 + NO -> MO2 + NO2 + (CO2)	8.10E-12*exp(270/T)
RCO3 + NO -> NO2 + ETO2	6.70E-12*exp(340/T)
MAO3 + NO -> NO2 + 0.5CH2O + 0.5CO + (CO2) + 0.5MO2 + 0.5MCO3	6.70E-12*exp(340/T)
ATO2 + NO -> 0.96NO2 + 0.960CH2O + 0.960MCO3 + 0.04R4N2	2.80E-12*exp(300/T)
RIO2 + HO2 -> 0.88RIP + 0.12OH + 0.047MACR + 0.073MVK + 0.12HO2 + 0.12CH2O	2.06E-13*exp(1300/T)
VRO2 + HO2 -> 0.1VRP + 0.68OH + 0.578GLYC + 0.578MCO3 + 0.187MEK + 0.102HO2 + 0.102CH2O + 0.102MGLY + 0.033RCHO	1.82E-13*exp(1300/T)
MRO2 + HO2 -> 1.0MRP	1.82E-13*exp(1300/T)
MAN2 + HO2 -> 0.075PROPNN + 0.075CO + 0.075HO2 + 0.075MGLY + 0.075CH2O + 0.075NO2 + 0.15OH + 0.85ISNP	1.82E-13*exp(1300/T)
IEPOXOO + HO2 -> 0.725HAC + 0.275GLYC + 0.275GLYX + 0.275MGLY + 1.125OH + 0.825HO2 + (0.200CO2) + 0.375CH2O + 0.074HCOOH + 0.251CO	2.06E-13*exp(1300/T)
DIBOO + HO2 -> 0.15HO2 + 0.15OH + 0.078GLYC + 0.078MGLY + 0.072HAC + 0.072GLYX + 0.85R4P	2.06E-13*exp(1300/T)
MAOPO2 + HO2 -> 1.0HAC + (1.0CO2) + 2.0OH	1.82E-13*exp(1300/T)
HC5OO + HO2 -> 0.1IAP + 0.9OH + 0.9MGLY + 0.9GLYC + 0.9HO2	2.06E-13*exp(1300/T)
ISOPNDO2 + HO2 -> 0.5OH + 0.035MACRN + 0.155HCOOH + 0.22HAC + 0.065ETHLN + 0.325CH2O + 0.170NO2 + 0.075GLYC + 0.155NO3 + 0.075PROPNN + 0.170MEK + 0.175HO2 + 0.5ISNP	2.06E-13*exp(1300/T)

ISOPNBO2 + HO2 -> 0.3GLYC + 0.3HAC + 0.2CH2O + 0.13MACRN + 0.07MVKN + 0.3NO2 + 0.2HO2 + 0.5OH + 0.5ISNP	2.06E-13*exp(1300/T)
MACRNO2 + HO2 -> 0.08ACTA + 0.08CH2O + 0.15NO3 + 0.07HCOOH + 0.07MGLY + 0.85HAC + 0.85NO2 + (0.93CO2) + 1.0OH	1.82E-13*exp(1300/T)
MOBAOO + HO2 -> 0.15OH + 0.15HO2 + 0.15RCHO + (0.15CO2) + 0.85R4P	2.06E-13*exp(1300/T)
MCO3 + HO2 -> 0.15ACTA + 0.15O3 + 0.44OH + 0.44MO2 + 0.41MAP	5.20E-13*exp(980/T)
RCO3 + HO2 -> 0.410RP + 0.150RCOOH + 0.150O3 + 0.440OH + 0.440ETO2	4.30E-13*exp(1040/T)
ATO2 + HO2 -> 0.15MCO3 + 0.15OH + 0.15CH2O + 0.85ATOOH	8.60E-13*exp(700/T)
KO2 + HO2 -> 0.15OH + 0.15ALD2 + 0.15MCO3 + 0.85ATOOH	1.82E-13*exp(1300/T)
MAO3 + HO2 -> 0.44OH + 0.15O3 + 0.59CH2O + 0.39MO2 + 0.41MAOP + 0.39CO	4.30E-13*exp(1040/T)
RIO2 + MO2 -> 1.1HO2 + 1.22CH2O + 0.280MVK + 0.180MACR + 0.3HC5 + 0.24MOH + 0.24ROH	8.37E-14
HC5OO + MO2 -> 0.50HO2 + 0.33CO + 0.09H2 + 0.18HAC + 0.13GLYC + 0.29MGLY + 0.25MEK + 0.95CH2O + 0.25MOH + 0.25ROH + 0.5HO2	8.37E-14
MRO2 + MO2 -> 0.595HAC + 0.255MGLY + 0.595CO + 1.255CH2O + 1.7HO2 + 0.150ROH	8.37E-14
VRO2 + MO2 -> 0.14HO2 + 0.14CH2O + 0.36MCO3 + 0.36GLYC + 0.14MGLY + 0.25MEK + 0.75CH2O + 0.25MOH + 0.25ROH + 0.5HO2	8.37E-14
MAN2 + MO2 -> 0.375PROPNN + 0.375CO + 0.375HO2 + 0.375MGLY + 0.375CH2O + 0.375NO2 + 0.250CH2O + 0.250R4N2	8.37E-14
MAOPO2 + MO2 -> 0.7HAC + (0.7CO2) + 0.7OH + 1.0CH2O + 0.7HO2 + 0.3ROH	8.37E-14
2RIO2 -> 1.28HO2 + 0.92CH2O + 0.56MVK + 0.36MACR + 0.48ROH + 0.5HC5	1.54E-13
2MAOPO2 -> 2.0HAC + (2.0CO2) + 2.0OH	8.37E-14
MCO3 + MO2 -> CH2O + MO2 + HO2	1.80E-12*exp(500/T)
MCO3 + MO2 -> ACTA + CH2O	2.00E-13*exp(500/T)
RCO3 + MO2 -> CH2O + HO2 + ETO2	1.68E-12*exp(500/T)
RCO3 + MO2 -> RCOOH + CH2O	1.87E-13*exp(500/T)
MAO3 + MO2 -> CH2O + HO2 + CH2O + MCO3	1.68E-12*exp(500/T)
MAO3 + MO2 -> RCOOH + CH2O	1.87E-13*exp(500/T)
MAOPO2 + MCO3 -> 1.0HAC + (2.0CO2) + OH + MO2	1.68E-12*exp(500/T)
MAOPO2 + MCO3 -> 1.0ACTA + 1.0MEK	1.87E-13*exp(500/T)
R4O2 + MCO3 -> MO2 + 0.32ACET + 0.19MEK + 0.27HO2 + 0.32ALD2 + 0.13RCHO + 0.05A3O2 + 0.18B3O2 + 0.32ETO2	1.68E-12*exp(500/T)
R4O2 + MCO3 -> 1.0ACTA + 1.0MEK	1.87E-13*exp(500/T)
ATO2 + MCO3 -> MCO3 + CH2O + MO2	1.68E-12*exp(500/T)
ATO2 + MCO3 -> MGLY + ACTA	1.87E-13*exp(500/T)
HC5OO + MCO3 -> 0.216GLYX + 0.234MGLY + 0.234GLYC + 0.216HAC + 0.29DHMOB + 0.17MOBA + 0.09RCHO + HO2 + 0.09CO + MO2	1.68E-12*exp(500/T)
HC5OO + MCO3 -> MEK + ACTA	1.87E-13*exp(500/T)
VRO2 + MCO3 -> 0.4HO2 + 0.4CH2O + 0.6MCO3 + 0.6GLYC + 0.4MGLY + 1.0MO2	1.68E-12*exp(500/T)

VRO2 + MCO3 -> MEK + ACTA	1.87E-13*exp(500/T)
MRO2 + MCO3 -> 0.850HO2 + 0.143MGLY + 0.857HAC + 0.857CO + 0.143CH2O + 1.0MO2	1.68E-12*exp(500/T)
MRO2 + MCO3 -> MEK + ACTA	1.87E-13*exp(500/T)
MAN2 + MCO3 -> 0.5PROPNN + 0.5CO + 0.5HO2 + 0.5MGLY + 0.5CH2O + 0.5NO2 + (CO2) + MO2	1.68E-12*exp(500/T)
MAN2 + MCO3 -> RCHO + ACTA + NO2	1.87E-13*exp(500/T)
RIO2 + MCO3 -> 0.887HO2 + 0.747CH2O + 0.453MVK + 0.294MACR + 0.140HC5 + 0.113DIBOO + (CO2) + MO2	1.68E-12*exp(500/T)
RIO2 + MCO3 -> MEK + ACTA	1.87E-13*exp(500/T)
MCO3 + MCO3 -> 2MO2	2.50E-12*exp(500/T)
RCO3 + MCO3 -> MO2 + ETO2	2.50E-12*exp(500/T)
MAO3 + MCO3 -> MO2 + MCO3 + CH2O	2.50E-12*exp(500/T)
MCO3 + NO2 -> PAN	8.59E-12
PAN -> MCO3 + NO2	5.73E-04
RCO3 + NO2 -> PPN	7.40E-12
PPN -> RCO3 + NO2	4.44E-04
MAO3 + NO2 -> PMN	7.40E-12
PMN -> MAO3 + NO2	4.44E-04
MACRNO2 + NO2 -> PMNN	7.40E-12
PMNN -> MACRNO2 + NO2	4.44E-04
ISOP + O3 -> 0.244MVK + 0.325MACR + 0.845CH2O + 0.110H2O2 + 0.522CO + 0.204HCOOH + 0.199MCO3 + 0.026HO2 + 0.270OH + 0.128PRPE + 0.051MO2	1.00E-14*exp(-1970/T)
MVK + O3 -> 0.202OH + 0.202HO2 + 0.352HCOOH + 0.535CO + 0.050ALD2 + 0.950MGLY + 0.050CH2O	8.50E-16*exp(-1520/T)
MACR + O3 -> 0.261OH + 0.202HO2 + 0.326HCOOH + 0.569CO + 0.880MGLY + 0.120CH2O	1.40E-15*exp(-2100/T)
HC5 + O3 -> 0.6MGLY + 0.1OH + 0.12CH2O + 0.28GLYC + 0.3O3 + 0.4CO + 0.2H2 + 0.2HAC + 0.2HCOOH	6.16E-15*exp(-1814/T)
ISOPNB + O3 -> 0.610MVKN + 0.390MACRN + 0.27OH + CH2O	1.06E-16
ISOPND + O3 -> 0.5PROPNN + 0.5ETHLN + 0.27OH + 0.5GLYC + 0.5HAC	5.30E-17
MOBA + O3 -> OH + HO2 + (CO2) + MEK	2.00E-17
PMN + O3 -> NO2 + 0.6CH2O + HO2	8.20E-18
RIO2 -> 2.0HO2 + 1.0CH2O + 0.5MGLY + 0.5GLYC + 0.5GLYX + 0.500HAC + 1.0OH	4.07E+08*exp(-7694/T)
MRO2 -> 1.0CO + 1.0HAC + 1.0OH	2.90E+07*exp(-5297/T)
C10H16 + OH -> TERPO2	1.20E-11*exp(444/T)
C10H16 + O3 -> .7OH + MVK + MACR + HO2	1.00E-15*exp(-732/T)
C10H16 + NO3 -> TERPO2 + NO2	1.20E-12*exp(490/T)
TERPO2 + NO -> .1ACET + MVK + MACR + NO2	4.20E-12*exp(180/T)
TERPO2 + HO2 -> TERPOOH	7.50E-13*exp(700/T)
TERPOOH + OH -> TERPO2	3.80E-12*exp(200/T)
O3 -> O2 + O1D	2.80E-04*exp(-1.75/cos(x))
O3 -> O2 + O	6.76E-04*exp(-0.30/cos(x))
H2O2 -> 2OH	2.10E-05*exp(-0.86/cos(x))
NO2 -> NO + O	1.71E-02*exp(-0.55/cos(x))
NO3 -> NO + O2	3.03E-02*exp(-0.22/cos(x))

NO3 -> NO2 + O	2.49E-01*exp(-0.25/cos(x))
N2O5 -> NO3 + NO + O	1.02E-06*exp(-5.50/cos(x))
N2O5 -> NO3 + NO2	1.25E-04*exp(-0.85/cos(x))
HNO3 -> OH + NO2	2.8E-06*exp(-1.20/cos(x))
HO2NO2 -> HO2 + NO2	2.05E-05*exp(-1.20/cos(x))
CH2O -> 2HO2 + CO	1.05E-04*exp(-1.00/cos(x))
CH2O -> H2 + CO	1.25E-04*exp(-0.80/cos(x))
MP -> CH2O + HO2 + OH	1.65E-05*exp(-0.88/cos(x))
ALD2 -> MO2 + HO2 + CO	2.95E-05*exp(-1.40/cos(x))
ALD2 -> CH4 + CO	1.25E-08*exp(-6.00/cos(x))
PAN -> 0.6MCO3 + 0.6NO2 + 0.4MO2 + 0.4NO3	2.5E-06*exp(-1.00/cos(x))
RCHO -> ETO2 + HO2 + CO	7.35E-05*exp(-1.10/cos(x))
ACET -> MCO3 + MO2	3.76E-06*exp(-1.80/cos(x))
MEK -> 0.85MCO3 + 0.85ETO2 + 0.15MO2 + 0.15RCO3	3.05E-05*exp(-1.20/cos(x))
GLYC -> CH2O + 2.0HO2 + CO	2.20E-05*exp(-1.20/cos(x))
GLYX -> 2.0CO + 2.0HO2	1.16E-04*exp(-0.45/cos(x))
MGLY -> MCO3 + CO + HO2	2.60E-04*exp(-0.60/cos(x))
MVK -> PRPE + CO	6.72E-06*exp(-0.77/cos(x))
MVK -> MCO3 + CH2O + CO + HO2	2.24E-06*exp(-0.77/cos(x))
MVK -> MO2 + MAO3	2.24E-06*exp(-0.77/cos(x))
MACR -> MAO3 + HO2	5.85E-06*exp(-0.60/cos(x))
MACR -> CO + HO2 + CH2O + MCO3	5.85E-06*exp(-0.60/cos(x))
HAC -> MCO3 + CH2O + HO2	4.05E-06*exp(-1.10/cos(x))
INPN -> OH + HO2 + RCHO + NO2	1.65E-05*exp(-0.88/cos(x))
PRPN -> OH + HO2 + RCHO + NO2	1.65E-05*exp(-0.88/cos(x))
ETP -> OH + HO2 + ALD2	1.65E-05*exp(-0.88/cos(x))
RA3P -> OH + HO2 + RCHO	1.65E-05*exp(-0.88/cos(x))
RB3P -> OH + HO2 + ACET	1.65E-05*exp(-0.88/cos(x))
R4P -> OH + HO2 + RCHO	1.65E-05*exp(-0.88/cos(x))
PP -> OH + HO2 + ALD2 + CH2O	1.65E-05*exp(-0.88/cos(x))
RP -> OH + HO2 + ALD2	1.65E-05*exp(-0.88/cos(x))
RIP -> OH + HO2 + 0.710CH2O + 0.425MVK + 0.285MACR + 0.29HC5	1.65E-05*exp(-0.88/cos(x))
IAP -> OH + HO2 + 0.67CO + 0.190H2 + 0.36HAC + 0.26GLYC + 0.580MGLY	1.65E-05*exp(-0.88/cos(x))
ISNP -> OH + HO2 + RCHO + NO2	1.65E-05*exp(-0.88/cos(x))
VRP -> OH + 0.3HO2 + 0.3CH2O + 0.7MCO3 + 0.7GLYC + 0.3MGLY	1.65E-05*exp(-0.88/cos(x))
MRP -> OH + HO2 + HAC + CO + CH2O	1.65E-05*exp(-0.88/cos(x))
MAOP -> OH + CH2O + MCO3	1.65E-05*exp(-0.88/cos(x))
R4N2 -> NO2 + 0.320ACET + 0.190MEK + 0.180MO2 + 0.270HO2 + 0.320ALD2 + 0.130RCHO + 0.050A3O2 + 0.180B3O2 + 0.320ETO2	3.94E-06*exp(-1.20/cos(x))
MAP -> OH + MO2	1.65E-05*exp(-0.88/cos(x))
MACRN -> NO2 + HAC + MGLY + 0.5CH2O + HO2 + 0.5CO	3.50E-4*exp(-1.00/cos(x))
MVKN -> GLYC + NO2 + MCO3	2.50E-06*exp(-1.00/cos(x))
ISOPNB -> HC5 + NO2 + HO2	2.50E-06*exp(-1.00/cos(x))
ISOPND -> HC5 + NO2 + HO2	2.50E-06*exp(-1.00/cos(x))
PROPNN -> CH2O + NO2 + CO + MO2	2.50E-06*exp(-1.00/cos(x))
ATOOH -> OH + CH2O + MCO3	1.65E-05*exp(-0.88/cos(x))

Table S4. The relationship between solar zenith angle (sza) and photolysis rates (j = a*exp(b/cos(sza))), which are obtained from the TUV radiation model. Adjusted R^2 indicates the adjusted correlation coefficient for each curve fitting result. The last two columns show the photolysis rates obtained from TUV simulations and NCAR C-130 observations at 10:37 CST (which corresponds to sza of 0.32), respectively. J-value observations onboard NCAR C-130 over the AABC and SEARCH sites are available on 06/14/2013. The j-values collected below pressure altitude of 1000 m while over the two ground sites are averaged and used here (sampling time ranges between 10:02 CST and 11:11 CST with middle sampling time at 10:37 CST). NA indicates no observations were available for the specific reaction.

Number	Reaction	a	b	Adjusted R^2	TUV (s-1)	C-130 (s-1)
R_01	O3 -> O2 + O(1D)	2.80E-4	-1.75	0.996	4.47E-05	3.74E-05
R_02	O3 -> O2 + O(3P)	6.76E-4	-0.30	0.996	4.92E-04	NA
R_03	H2O2 -> 2 OH	2.10E-5	-0.86	0.993	8.42E-06	7.96E-06
R_04	NO2 -> NO + O(3P)	1.88E-2	-0.50	0.999	1.11E-02	9.48E-03
R_05	NO3 -> NO + O2	3.03E-2	-0.22	0.998	2.40E-02	NA
R_06	NO3 -> NO2 + O(3P)	2.49E-1	-0.25	0.999	1.91E-01	NA
R_07	N2O5 -> NO3 + NO + O(3P)	1.02E-6	-5.50	0.998	3.03E-09	NA
R_08	N2O5 -> NO3 + NO2	1.25E-4	-0.85	0.994	5.09E-05	4.73E-05
R_09	HNO2 -> OH + NO	3.85E-3	-0.50	0.995	2.26E-03	1.54E-03
R_10	HNO3 -> OH + NO2	2.80E-6	-1.20	0.993	7.93E-07	6.82E-07
R_11	HNO4 -> HO2 + NO2	2.05E-5	-1.20	0.995	5.80E-06	7.22E-06
R_12	CH2O -> H + HCO	1.05E-4	-1.00	0.996	3.68E-05	3.53E-05
R_13	CH2O -> H2 + CO	1.25E-4	-0.80	0.990	5.37E-05	5.38E-05
R_14	CH3CHO -> CH3 + HCO	2.95E-5	-1.40	0.996	6.74E-06	5.79E-06
R_15	CH3CHO -> CH4 + CO	1.25E-8	-6.00	0.992	2.16E-11	NA
R_16	C2H5CHO -> C2H5 + HCO	7.35E-5	-1.10	0.988	2.28E-05	1.94E-05
R_17	CH2(OH)CHO -> Products	2.20E-5	-1.20	0.995	6.23E-06	NA
R_18	CH2=C(CH3)CHO -> Products	1.17E-5	-0.60	0.996	6.21E-06	NA
R_19	CH3COCH3 -> CH3CO + CH3	3.76E-6	-1.80	0.992	5.61E-07	1.20E-06
R_20	CH3COCHCH2 -> Products	1.12E-5	-0.77	0.991	4.92E-06	NA
R_21	CH3COCH2CH3 -> CH3CO + CH2CH3	3.05E-5	-1.20	0.994	8.52E-06	7.26E-06
R_22	CH2(OH)COCH3 -> CH3CO + CH2(OH)	4.05E-6	-1.10	0.990	1.26E-06	NA
R_23	CH3OOH -> CH3O + OH	1.65E-5	-0.88	0.991	6.44E-06	NA
R_24	CH3CO(OOH) -> Products	2.74E-6	-1.00	0.994	9.68E-07	NA
R_25	CH3ONO2 -> CH3O + NO2	3.94E-6	-1.20	0.994	1.12E-06	NA
R_26	CH3CO(OONO2) -> CH3CO(OO) + NO2	1.51E-6	-1.00	0.992	5.26E-07	5.54E-07
R_27	CH3CO(OONO2) -> CH3CO(O) + NO3	1.00E-6	-1.00	0.993	3.51E-07	2.37E-07
R_28	CH3CH2CO(OONO2) -> CH3CH2CO(OO) + NO2	2.50E-6	-1.00	0.992	8.68E-07	NA

R_29	CHOCHO -> HCO + HCO	1.16E-4	-0.45	0.998	7.22E-05	7.59E-05
R_30	CH3COCHO -> CH3CO + HCO	2.60E-4	-0.60	0.996	1.38E-04	1.45E-04

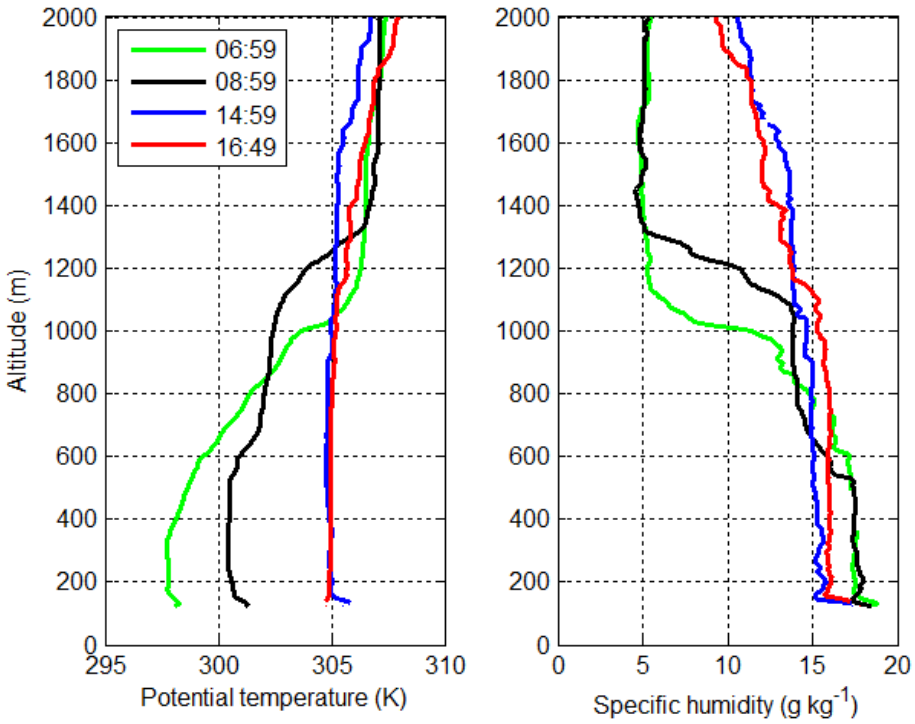

Figure S1. Vertical profiles of potential temperature and specific humidity collected from the sounding system at the SEARCH site on 2013-06-11. Time series shown in the legend are in CST format.

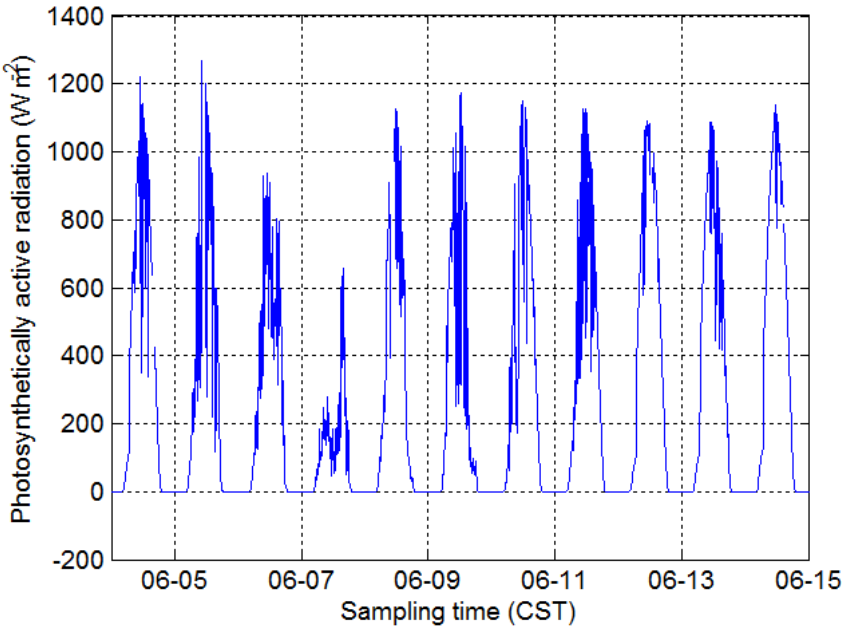

Figure S2. Photosynthetically active radiation (PAR) measured at 32 m on the AABC flux tower.

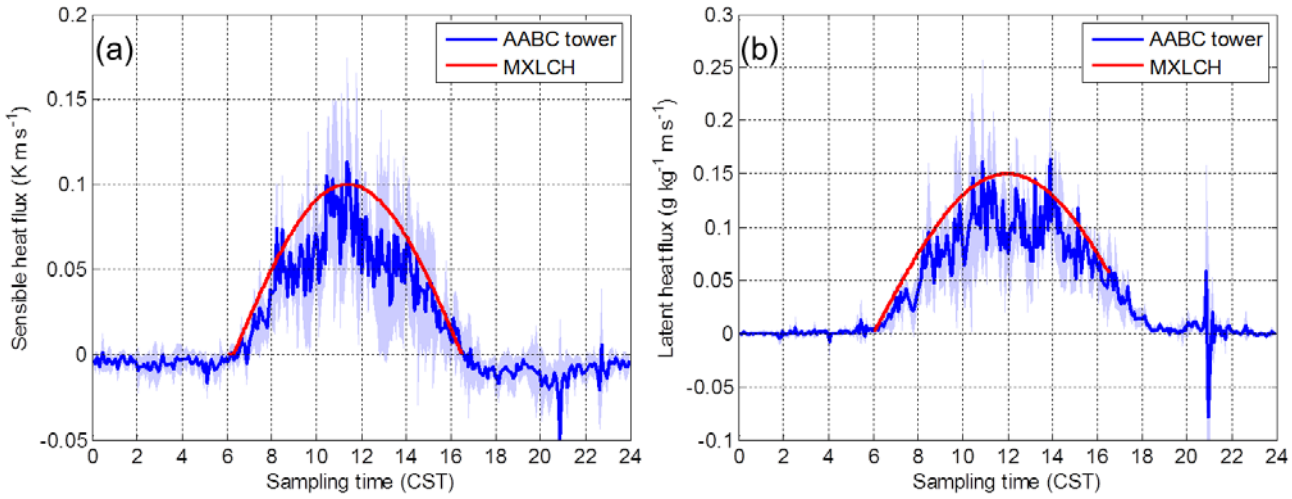

Figure S3. Diurnal evolution of (a) surface sensible heat flux, (b) surface latent heat flux. The blue lines indicate the averaged data obtained from the AABC tower over the low cloud cover days (June 10-13). The shaded areas indicate 1 standard deviation of the observations. The red line indicates the fitted curve, which is prescribed to MXLCH.

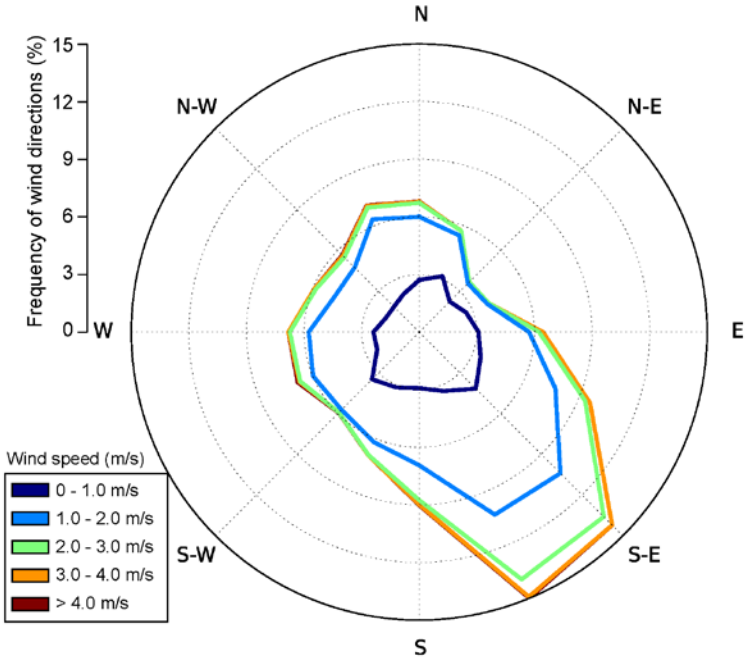

Figure S4. Summary of the horizontal wind data during 06:00-16:30 CST of the selected days (June 5, 6, 8, 10-13, 2013). The wind data were collected on top of the AABC flux tower at 44 m height above the ground level.

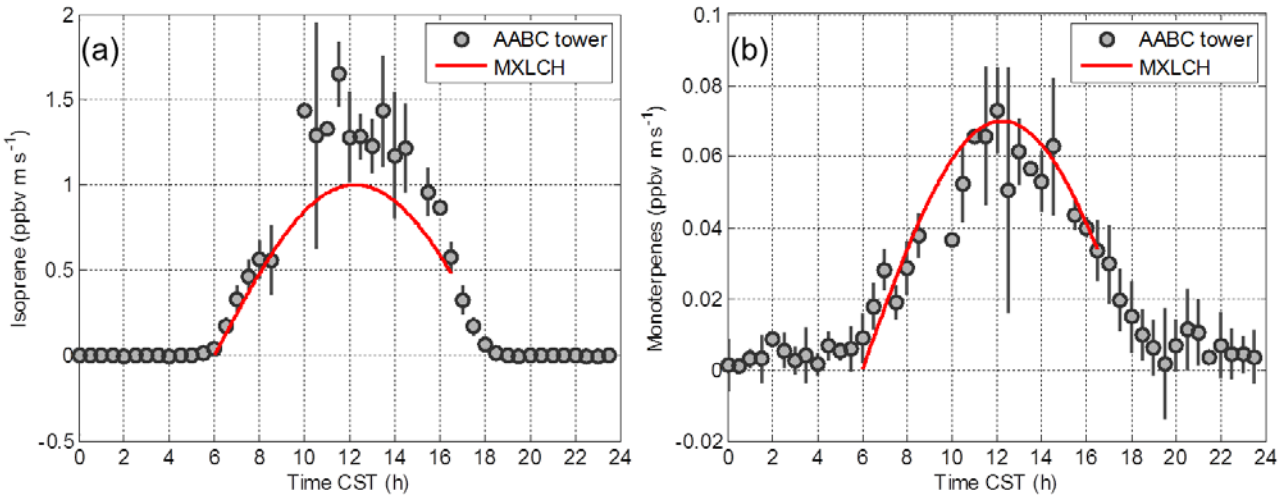

Figure S5. Diurnal evolution of (a) isoprene flux, (b) monoterpenes fluxes. The circles indicate averaged flux during within the time bin (30 min). Error bars indicate 1 standard deviation. The red line indicates the fitted curve, which is prescribed to MXLCH. The isoprene peak flux value prescribed in MXLCH is on the lower bound of the observations.

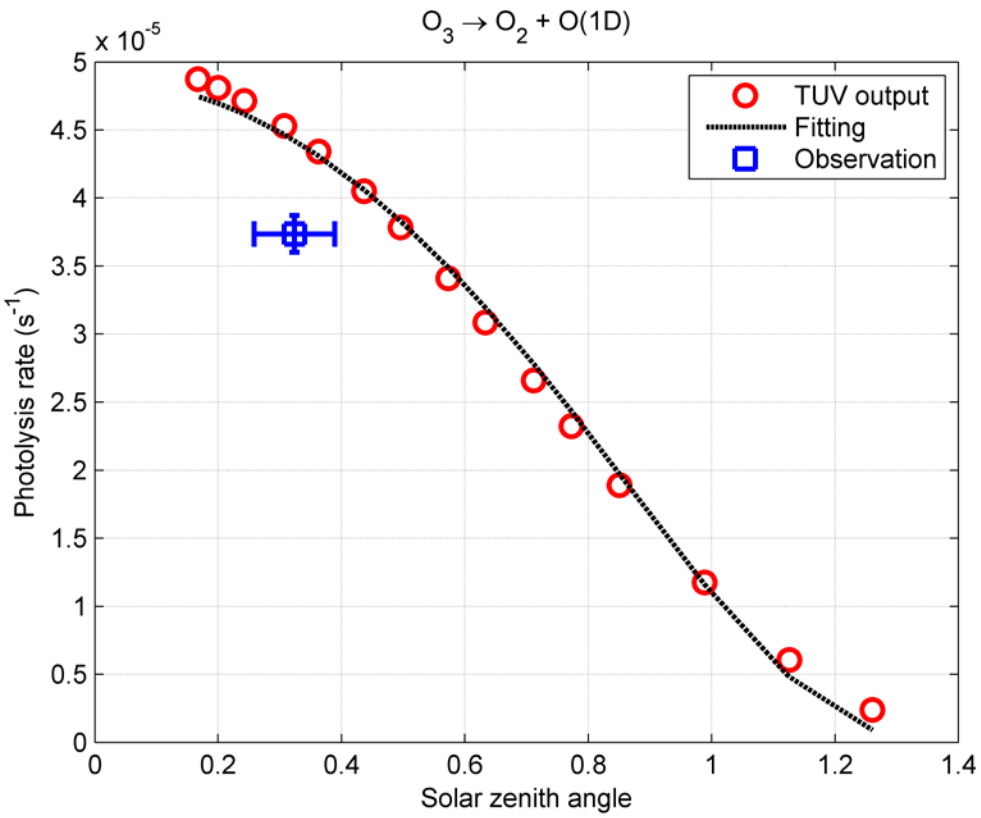

Figure S6. Comparison of TUV outputs with observation for photolysis reaction O3 -> O2 + O(1D). Error bars indicate 1 standard deviation. See Table S4 for curve fitting parameters and methods of processing the observational data.

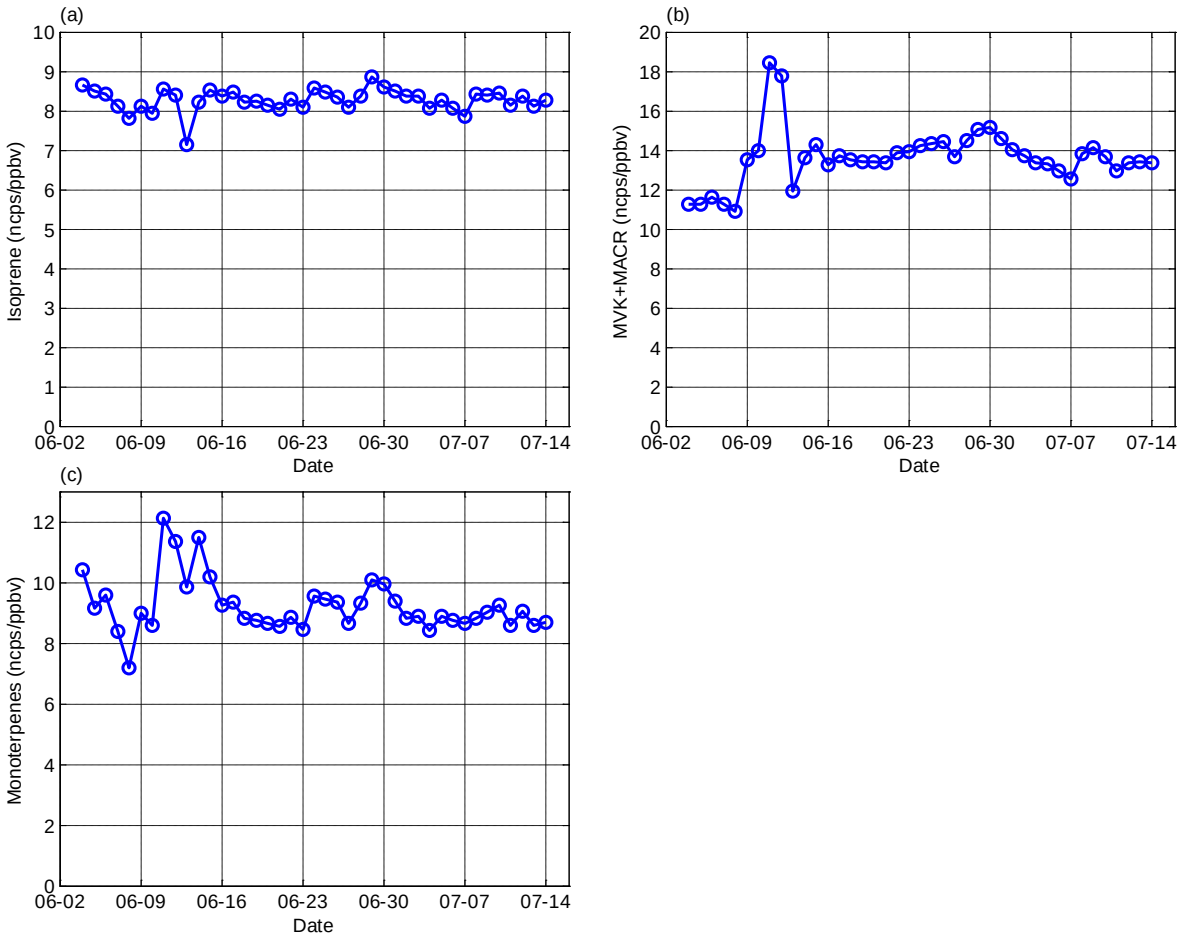

Figure S7. Summary of the sensitivities for (a) isoprene, (b) MVK+MACR, and (c) monoterpenes obtained from standard gas calibrations during the whole campaign period.

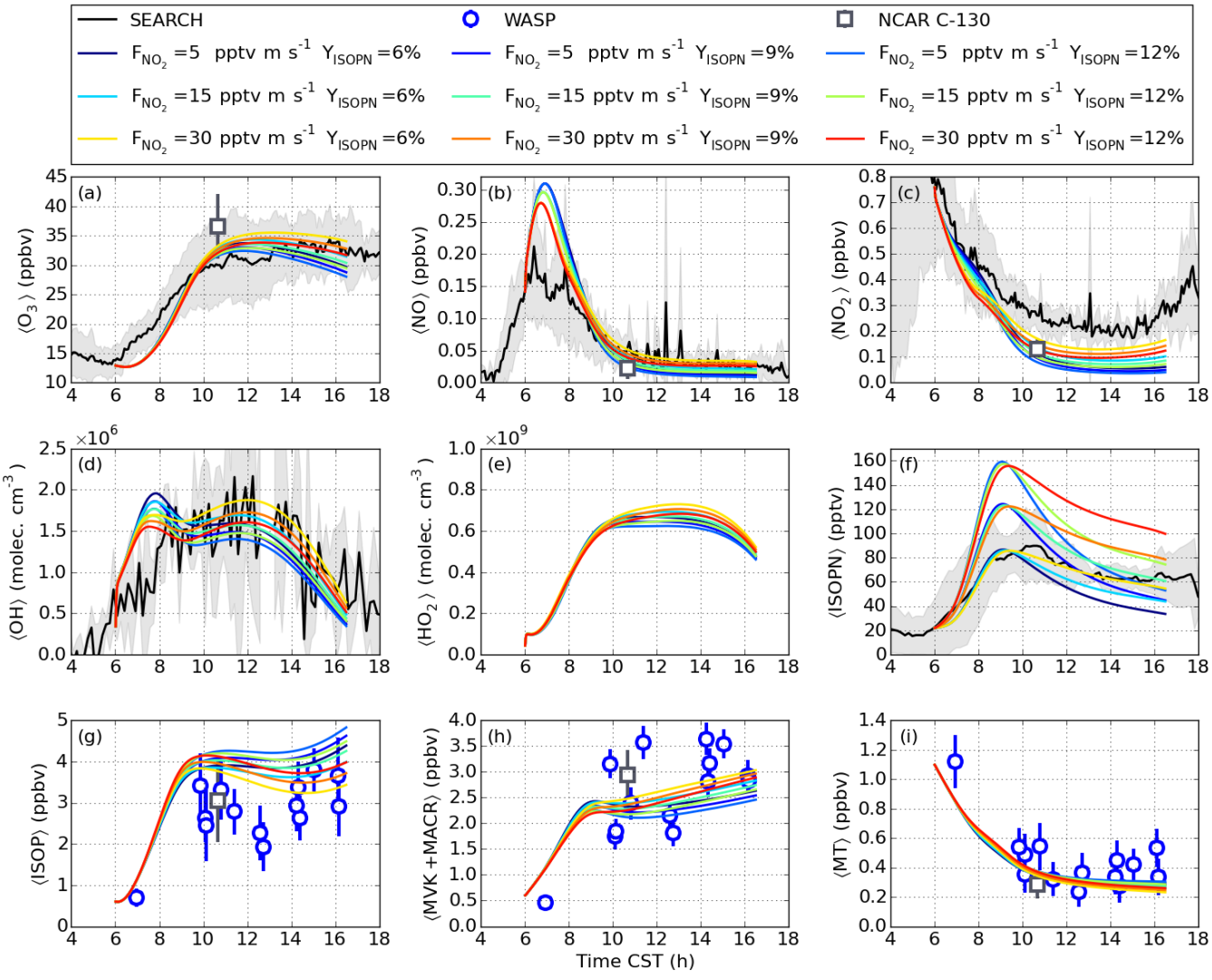

Figure S8. Comparison of observations with MXLCH outputs of different NOx flux levels and ISOPN yields. For each NO2 flux level, the NO flux is downward and takes the same magnitude, i.e., F_{NO2} = 5 ppbv m s^{-1} corresponds to F_{NO} = -5 ppbv m s^{-1}. See Figure 5 for denotion of observations.

References

Li, J. W.: Development and evaluation of flexible empirical peak functions for processing chromatographic peaks, Anal Chem, 69, 4452-4462, Doi 10.1021/Ac970481d, 1997.