

Supplemental Material

S1 – UBWOS 2012 data used in this analysis

(all data available at <http://www.esrl.noaa.gov/csd/groups/csd7/measurements/2012ubwos/Ground>)

Measurement	Technique	Data frequency used	Approximate Inlet height
O ₃	Cavity ring-down	60 s	11 m
O ₃	UV absorption	60 s	13 m
NO ₂ / NO	Cavity ring-down	60 s	11 m
HCHO	PTR-MS	60 s	11 m
ClNO ₂	CIMS	60 s	11 m
HONO	CIMS	60 s	11 m
$j(\text{O}^1\text{D}) / j(\text{NO}^2)$	Filter radiometers	60 s	10 m
CO	V-UV fluorescence	60 s	13 m
VOCs	GC-MS	5 min sample, 30 min frequency	11 m
Methane	Picarro Cavity ring-down	60 s	11 m
Relative humidity	Vaisala HMP45C	60 s	13 m
Wind speed	RMYoung propvane	60 s	13 m
Temperature		60 s	13 m
Pressure	Vaisala PTB101B	60 s	13 m

S2 – Model constraints

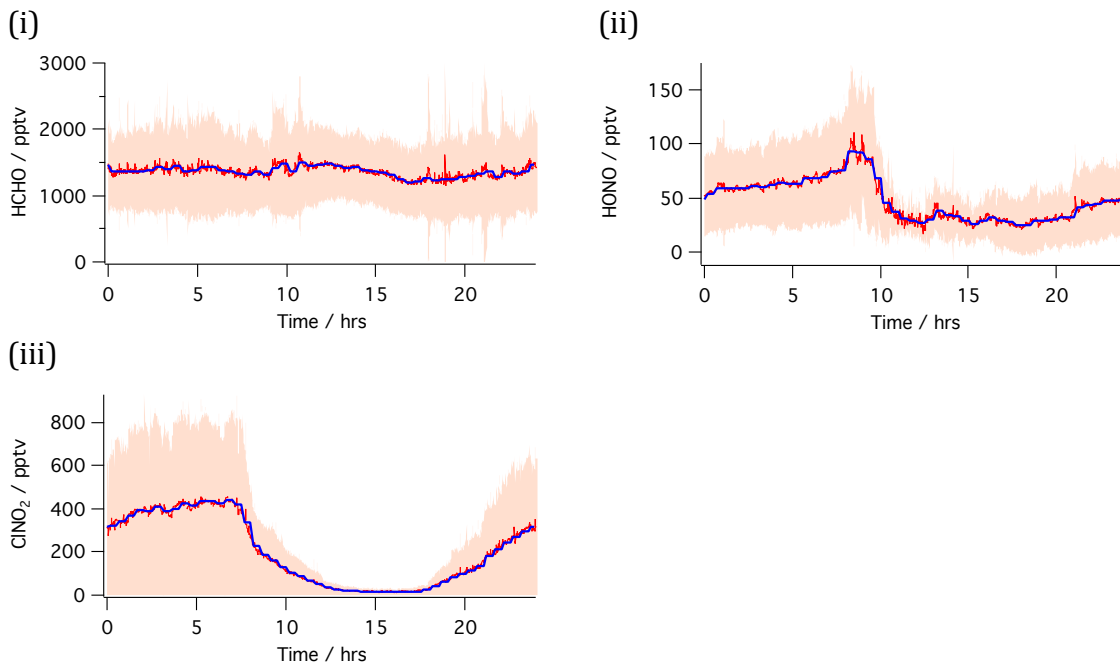
(a) Parameters constrained to a fixed value

Species / parameter	Value	Comments
Methane	3.4669 ppmV	Campaign median
Water vapour	3626.8 ppmV	Calculated mean from RH
Isoprene	0.87 pptV	Campaign mean as concentrations showed very little variability and were close to limit of detection
Styrene	0.06 pptV	
Benzaldehyde	11.98 pptV	
DMS	0.51 pptV	
CO	182.84 ppbV	Campaign median
Pressure	830 hPa	Campaign mean

(b) Radical precursors

Red = 1 minute campaign average diurnal observations, after wind filter has been applied (S3), with shading indicating ± 1 standard deviation

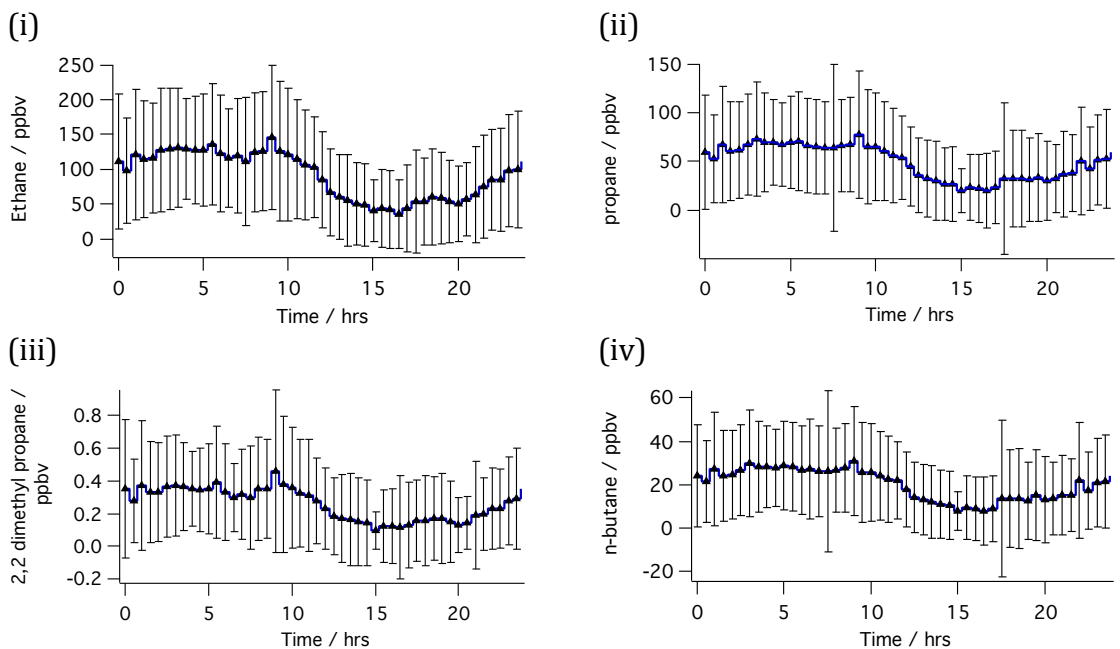
Blue = 30 minute average model constraint



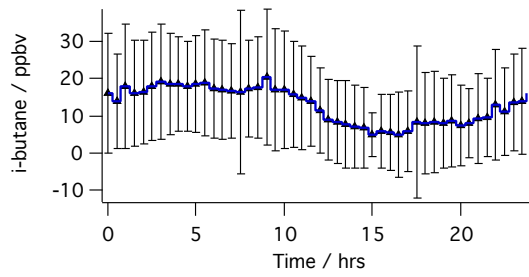
(c) Alkanes that were constrained to observed diurnal profiles

Black = 30 minute average observations, after wind filter has been applied (S3), with error bars indicating ± 1 standard deviation

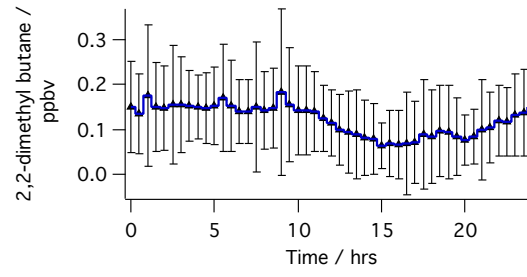
Blue = 30 minute average model constraint



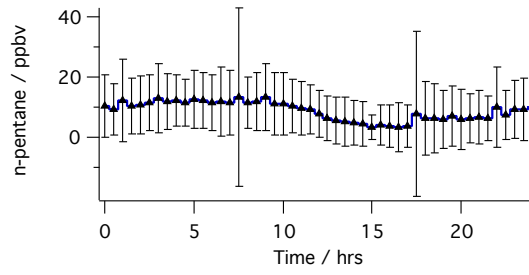
(v)



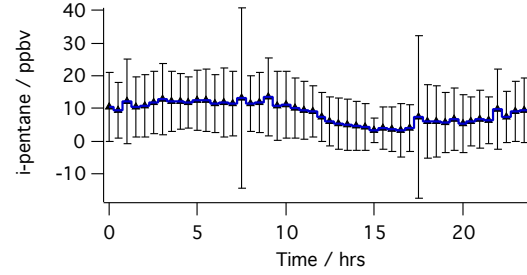
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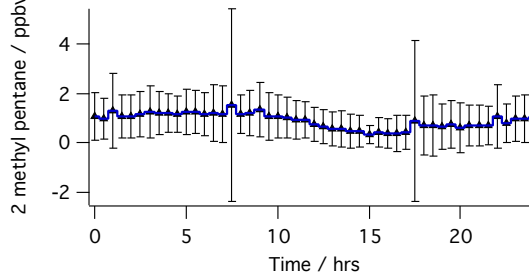
(vii)



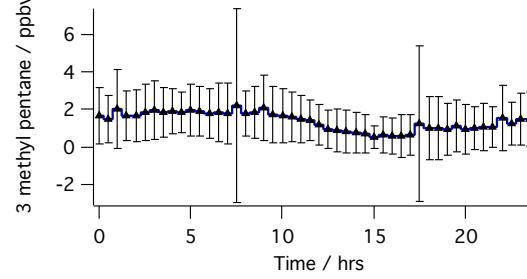
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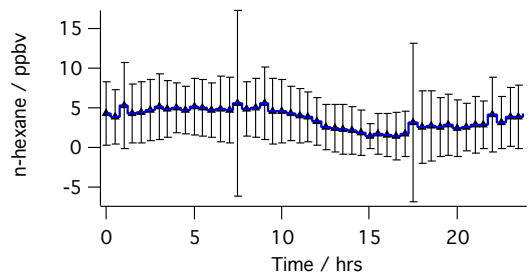
(ix)



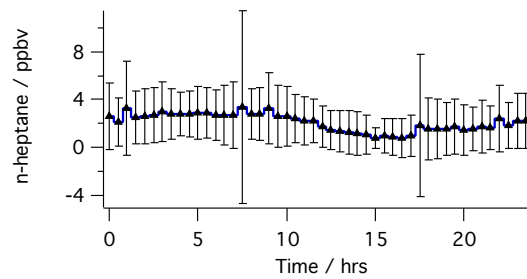
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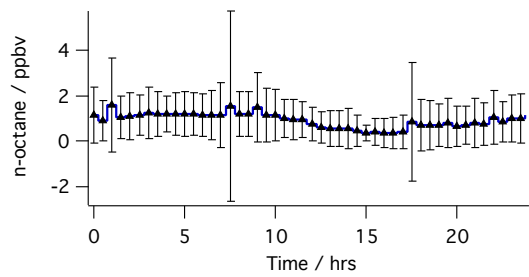
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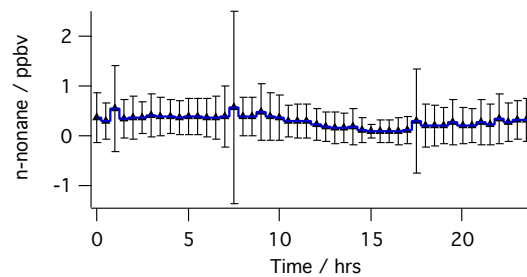
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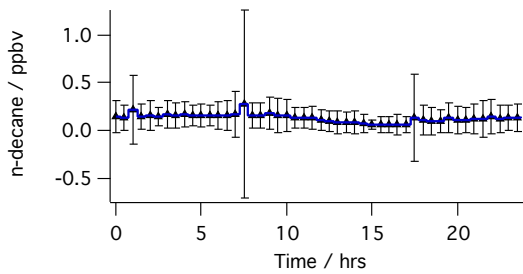
(xiii)



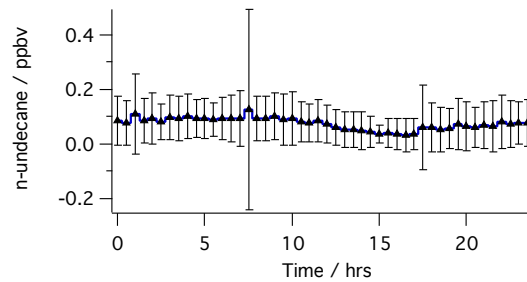
(xiv)



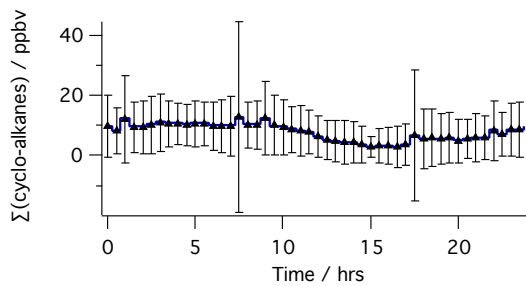
(xv)



(xvi)



(xvii)



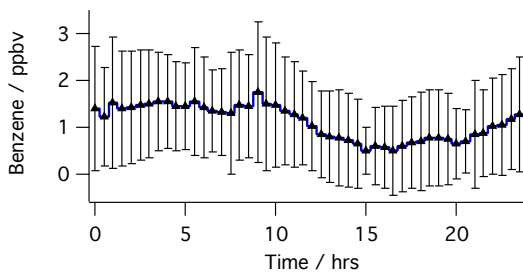
$\Sigma(\text{cyclo-alkanes}) = (\text{Cyclohexane}) + (1\text{-ethyl cyclohexane}) + (1\text{-methyl cyclohexane}) + (\text{trans } 1,3\text{-dimethyl cyclohexane}) + (1,1,3\text{-trimethyl cyclohexane}) + (\text{cis } 1,2\text{-dimethyl cyclohexane}) + (1\text{-methyl cyclopentane})$

(d) Aromatics that were constrained to observed diurnal profiles

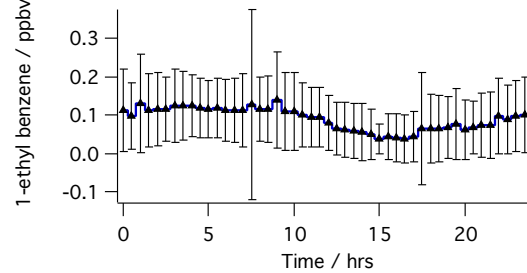
Black = 30 minute average observations, after wind filter has been applied (S3), with error bars indicating ± 1 standard deviation

Blue = 30 minute average model constraint

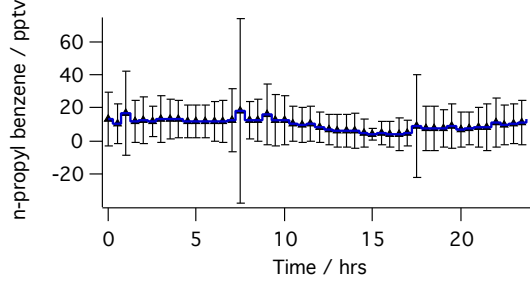
(i)



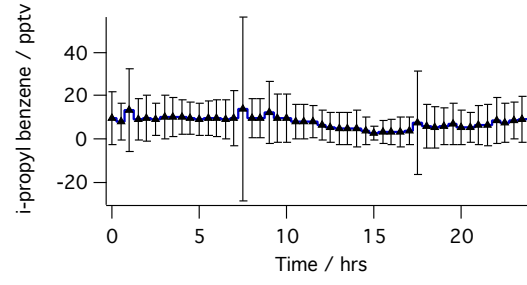
(ii)



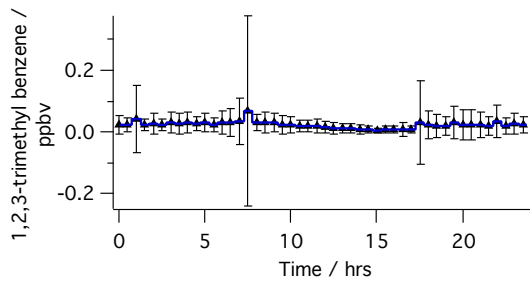
(iii)



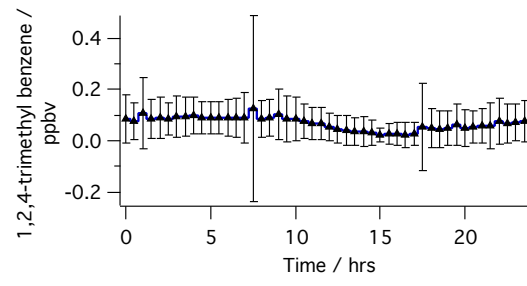
(iv)



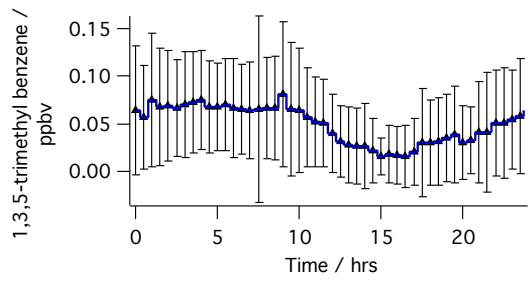
(v)



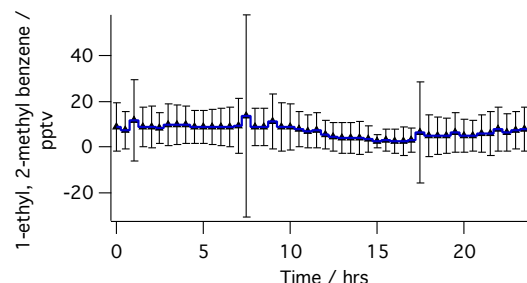
(vi)



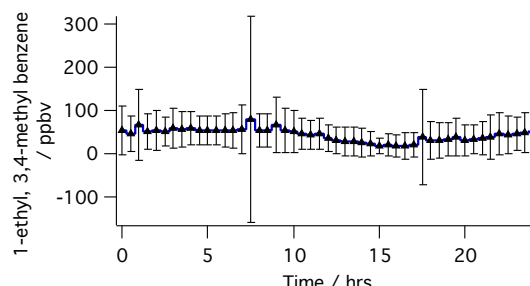
(vii)



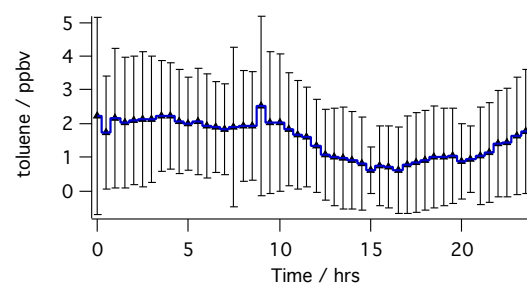
(viii)



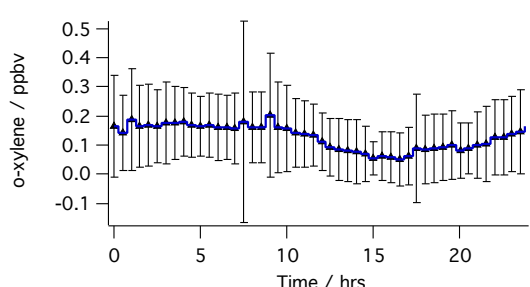
(ix)



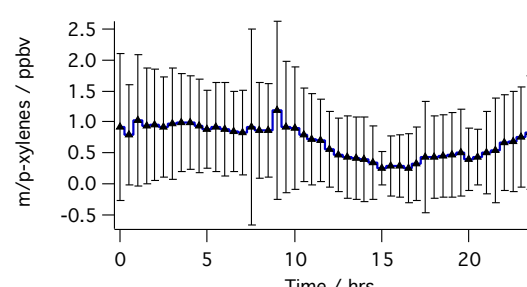
(x)



(xi)



(xii)

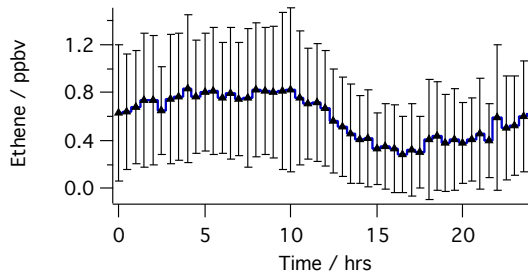


(e) Unsaturated hydrocarbons that were constrained to observed diurnal profiles (other measured alkenes (C2-C5) were generally below the instruments limit of detection (~ 1 pptv) throughout the campaign).

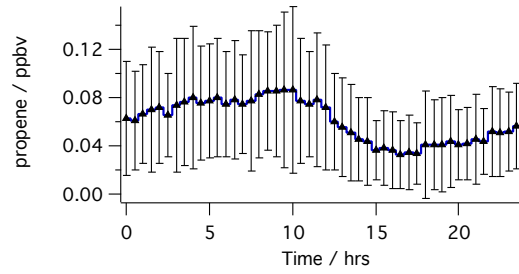
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Blue = 30 minute average model constraint

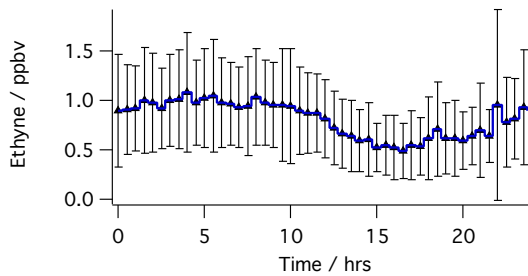
(i)



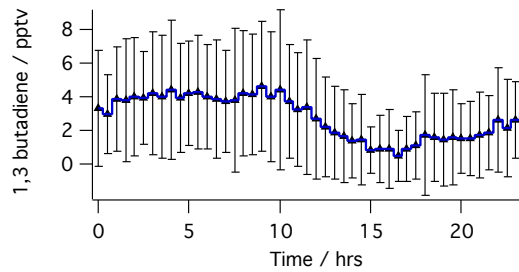
(ii)



(iii)

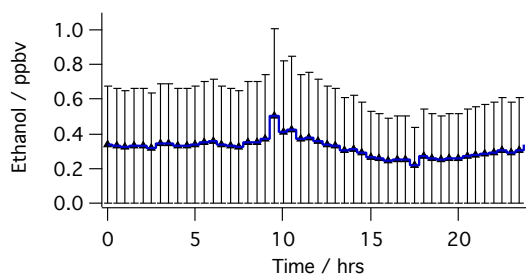


(iv)

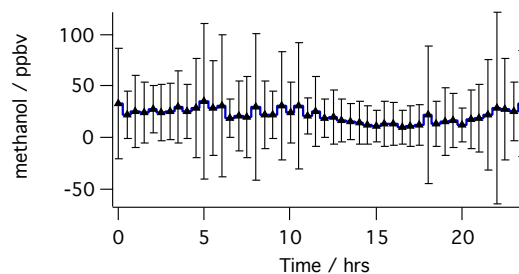


- (f) Oxygenates that were constrained to observed diurnal profiles
 Black = 30 minute average observations, after wind filter has been applied (S3), with error bars indicating ± 1 standard deviation
 Blue = 30 minute average model constraint

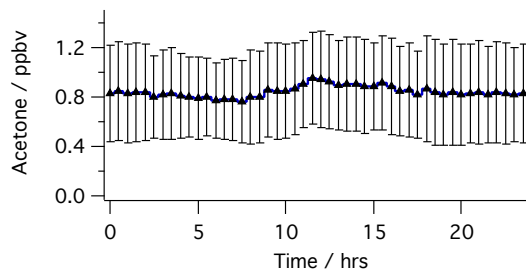
(i)



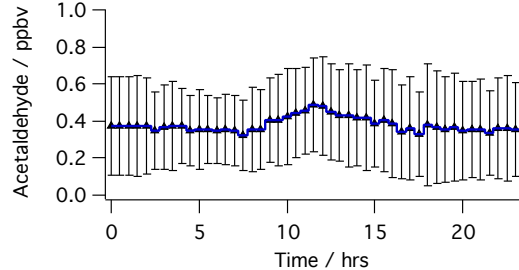
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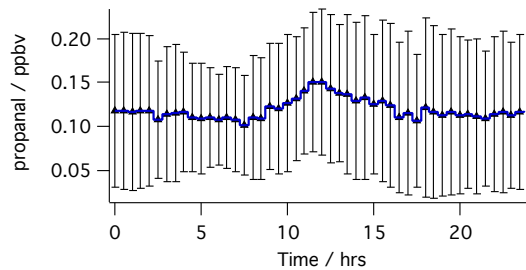
(iii)



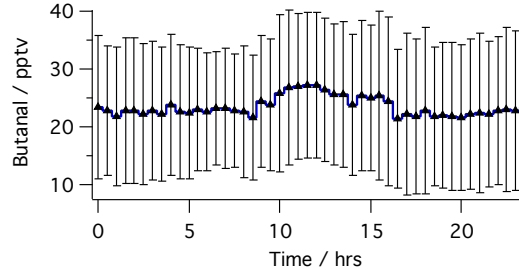
(iv)



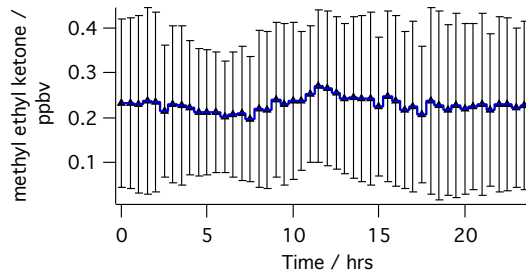
(v)



(vi)



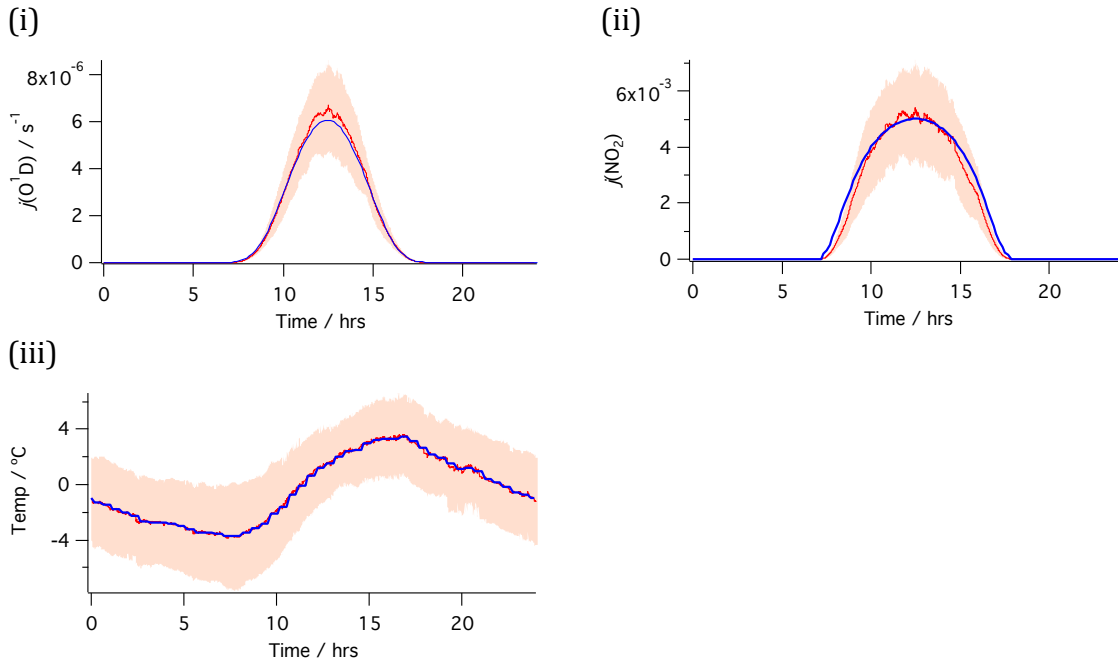
(vii)



(g) Physical parameters. Photolysis observations used to scale TUV calculated photolysis rates.

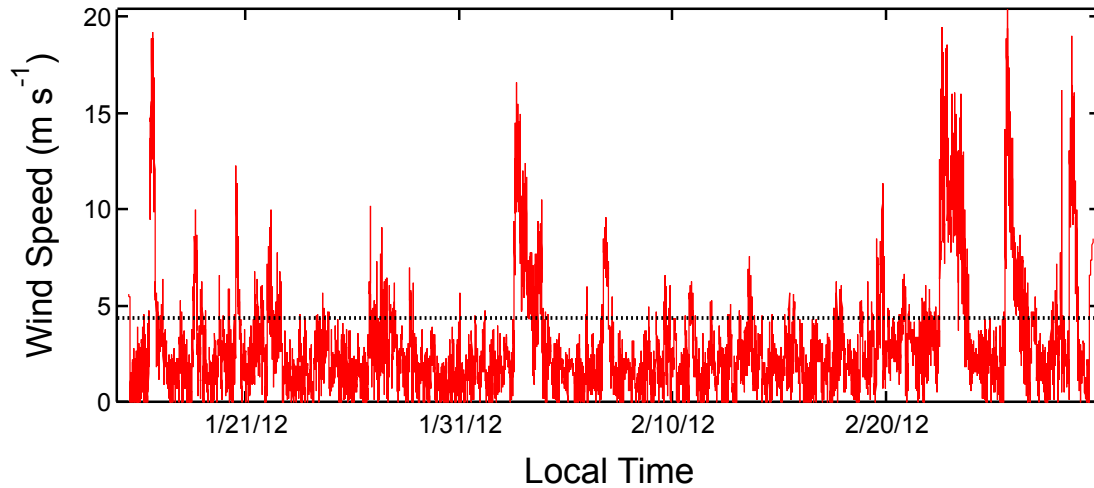
Red = 1 minute campaign average diurnal observations, after wind filter has been applied (S3), with shading indicating ± 1 standard deviation

Blue = (i) and (ii) TUV calculated photolysis, and (iii) 30 minute average temperature model constraint

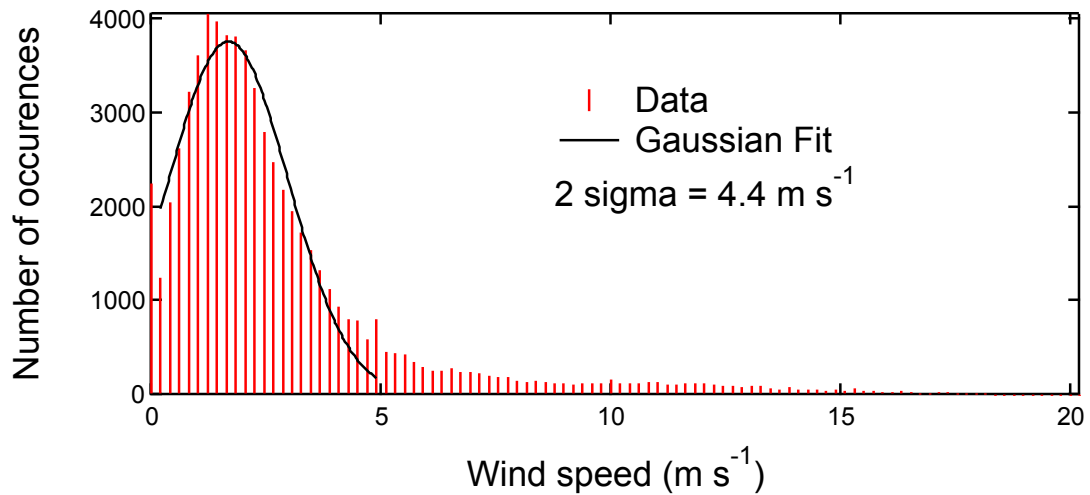


S3 All data used for model constraints and comparisons was first filtered at +2 sigma to remove high wind data.

(a) Wind speed time series (red), with +2 sigma filter (4.4 m s^{-1}) shown in black.



(b) Histogram of wind speed data used to determine filter used to remove high speed data.



S4 Chlorine reactions added to MCM v3.2 for sensitivity study described in Section 2.2. All reaction products have degradation schemes already within MCM v3.2.

Reaction	Rate	Reference
Inorganic		
OH + HCl --> Cl	1.8D-12*EXP(-250/TEMP)	Atkinson 2007 (IUPAC)
Cl + O ₃ --> ClO	2.3D-11*EXP(-200/TEMP)	Sander 2011 (JPL)
Cl + NO --> NOCl	7.6D-32*M*(TEMP/300)@-1.8	Sander 2011 (JPL)
ClO + NO --> Cl	6.2D-12*EXP(295/TEMP)	Atkinson 2007 (IUPAC)
OH + ClO --> Cl + HO ₂	7.4D-12*EXP(270/TEMP)	Atkinson 2007 (IUPAC)
OH + ClO --> HCl	6.0D-13*EXP(230/TEMP)	Atkinson 2007 (IUPAC)
HO ₂ + Cl --> HCl	1.4D-11*EXP(270/TEMP)	Atkinson 2007 (IUPAC)
HO ₂ + Cl --> OH + ClO	3.6D-11*EXP(-375/TEMP)	Atkinson 2007 (IUPAC)

Organic		
C ₂ H ₂ + Cl --> CHOCl + CO + HO ₂	6.1D-30*M*(TEMP/300)**-3*0.26	Sander 2011 (JPL)
C ₂ H ₂ + Cl --> GLYOX + HCL	6.1D-30*M*(TEMP/300)**-3*0.21	Sander 2011 (JPL)
C ₂ H ₂ + Cl --> CO +CO + HO ₂ + HCL	6.1D-30*M*(TEMP/300)**-3*0.53	Sander 2011 (JPL)
C ₂ H ₄ + Cl --> CH ₂ CLCH ₂ O ₂	1.85D-29*M*(TEMP/300)**-3.3	Sander 2011 (JPL)
C ₂ H ₅ OH + Cl --> CH ₃ CHO + HO ₂ + HCL	8.6D-11*EXP(45/TEMP)*0.92	Sander 2011 (JPL)
C ₂ H ₅ OH + Cl --> HOCH ₂ CH ₂ O ₂ + HCL	8.6D-11*EXP(45/TEMP)*0.08	Sander 2011 (JPL)
IPROPOL + Cl --> CH ₃ COCH ₃ + HO ₂ + HCL	8.6D-11*0.85	Atkinson 2006 (IUPAC)
IPROPOL + Cl --> IPROPOLO ₂ + HCL	8.6D-11*0.15	Atkinson 2006 (IUPAC)
CH ₃ OH + Cl --> HO ₂ + HCHO + HCL	8.6D-11*EXP(-167/TEMP)	Sander 2011 (JPL)
TOLUENE + Cl --> C ₆ H ₅ CH ₂ O ₂ + HCL	3.2D-11	Fantechi 1998
CL + HCHO --> HCL + CO + HO ₂	8.1D-11*EXP(-34/TEMP)	Sander 2011 (JPL)
CH ₃ COCH ₃ + Cl --> CH ₃ COCH ₂ O ₂ + HCL	3.2D-11*EXP(-815/TEMP)	Atkinson 2006 (IUPAC)