

Supplements

Tables in supplementary material

Table.S1. Detailed information of supporting measurements.

Species	Methods	limit of detection	Accuracy (1 σ)	Time resolution
OH	LIF ^a	$3.3 \times 10^5 \text{ cm}^{-3}$	$\pm 13 \%$	60 s
HO₂	LIF ^a	$1.1 \times 10^6 \text{ cm}^{-3}$	$\pm 17 \%$	60 s
Temperature	Met One 083E	-50 to 50 °C	$\pm 0.5 \%$	60 s
Relative humidity	Met One 083E	0–100 %	$\pm 2.0 \%$	60 s
WS	Met One 014A	0.45–60 m/s	$\pm 0.11 \text{ m/s}$	1 min
WD	Met One 024A	0–360° (>0.45 m/s)	$\pm 5^\circ$	1 min
Pressure	Met One 092	600–1100 hPa	$\pm 0.5 \%$	60 s
J-values	SR	-	$\pm 10 \%$	60 s
PM_{2.5}	TEOM	0.1 $\mu\text{g}/\text{m}^3$	$\pm 10 \%$	1 h
O₃	UV	0.5 ppb	$\pm 10 \%$	60 s
NO	CL	0.5 ppb	$\pm 10 \%$	60 s
NO₂	CL	1 ppb	$\pm 10 \%$	60 s
SO₂	UV-F	0.3 ppb	$\pm 10 \%$	60 s
CO	NDIR	50 ppb	$\pm 10 \%$	60 s
HONO	LOPAP	150 ppt	$\pm 15 \%$	60 s
HCHO	Hantzsch	200 ppt	$\pm 5 \%$	60 s
NMHCs	GC-MS/FID	5–70 ppt	$\pm 10\text{--}15 \%$	1 h

Table.S2. Photolysis frequencies for Br-related species (Atkinson et al., 2007; Bloss et al., 2010).

Reaction	Quantum Yield	Mean $j(x) / j(\text{NO}_2)$	References
$\text{Br}_2 + h\nu$		3.45	(Atkinson et al., 2007)
$\text{BrO} + h\nu$		5.41	(Atkinson et al., 2007)
$\text{BrONO}_2 + h\nu$	$\varphi(\text{Br} + \text{NO}_3)=1$	0.16	(Atkinson et al., 2007)
$\text{BrONO} + h\nu$	$\varphi(\text{Br} + \text{NO}_2)=0.5, \varphi(\text{BrO} + \text{NO})=0.5$	2.28	(Atkinson et al., 2007)
$\text{HOBr} + h\nu$		0.256	(Atkinson et al., 2007)

Table.S3. Gas-phase kinetics for Br-related species in RACM2 mechanism. Revised by (Bloss et al., 2010).

Reaction	Reaction rate constant (cm^3s^{-1})	References
$\text{Br} + \text{O}_3 \rightarrow \text{BrO} + \text{O}_2$	$1.7 \times 10^{-11} \exp(-800/T)$	(Atkinson et al., 2007)
$\text{Br} + \text{HO}_2 \rightarrow \text{HBr} + \text{O}_2$	$7.7 \times 10^{-12} \exp(-450/T)$	(Atkinson et al., 2007)
$\text{HBr} + \text{OH} \rightarrow \text{Br} + \text{H}_2\text{O}$	$6.7 \times 10^{-12} \exp(155/T)$	(Atkinson et al., 2007)
$\text{Br}_2 + \text{OH} \rightarrow \text{HOBr} + \text{Br}$	$2.0 \times 10^{-11} \exp(240/T)$	(Atkinson et al., 2007)
$\text{Br} + \text{HCHO} \rightarrow \text{HBr} + \text{HCO}$	$7.7 \times 10^{-12} \exp(-580/T)$	(Atkinson et al., 2007)
$\text{Br} + \text{ACD} \rightarrow \text{HBr} + \text{ACO}_3$	$1.8 \times 10^{-11} \exp(-460/T)$	(Atkinson et al., 2007)
$\text{Br} + \text{NO}_2 \rightarrow \text{BrONO}$	$k_0 = 4.2 \times 10^{-31} \exp(T/300)^{-2.4}$ $k_\infty = 2.7 \times 10^{-11}, F_c = 0.6$	(Bloss et al., 2010)
$\text{BrO} + \text{BrO} \rightarrow \text{Br} + \text{Br} + \text{O}_2$	2.7×10^{-12}	(Atkinson et al., 2007)
$\text{BrO} + \text{BrO} \rightarrow \text{Br}_2 + \text{O}_2$	$2.9 \times 10^{-14} \exp(840/T)$	(Atkinson et al., 2007)
$\text{BrO} + \text{HO}_2 \rightarrow \text{HOBr} + \text{O}_2$	$4.5 \times 10^{-12} \exp(500/T)$	(Atkinson et al., 2007)
$\text{HO} + \text{HOBr} \rightarrow \text{BrO} + \text{H}_2\text{O}$	5.0×10^{-11}	(Bloss et al., 2010)
$\text{BrO} + \text{MO}_2 \rightarrow \text{HOBr} + \text{HO}_2 + \text{HCHO}$	$4.6 \times 10^{-13} \exp(798/T)$	(Enami et al., 2007)
$\text{BrO} + \text{NO} \rightarrow \text{Br} + \text{NO}_2$	$8.7 \times 10^{-12} \exp(260/T)$	(Atkinson et al., 2007)
$\text{BrO} + \text{NO}_2 \rightarrow \text{BrONO}_2$	$k_0 = 5.2 \times 10^{-31} \exp(T/300)^{-3.2}$ $k_\infty = 6.9 \times 10^{-12} \exp(T/300)^{-2.9}, F_c = 0.6$	(Bloss et al., 2010)
$\text{BrONO}_2 \rightarrow \text{BrO} + \text{NO}_2$	$2.8 \times 10^{13} \exp(12360/T)$	(Orlando and Tyndall, 1996)

Figures in supplementary material

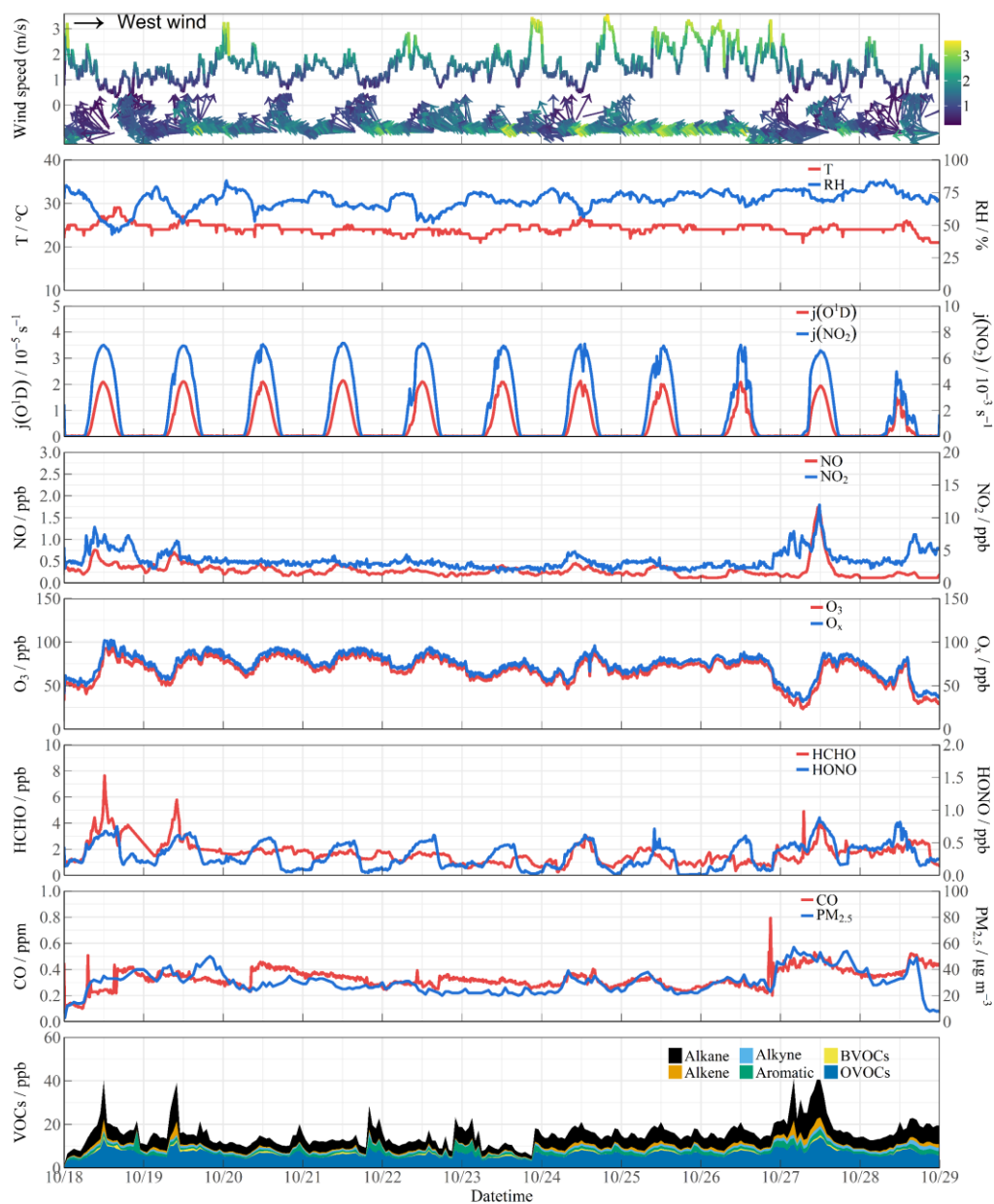


Fig. S1. Time series of observed meteorological and chemical parameters at YMK from 18 October to October 28, 2019. The GC-MS instrument failed between 24 and 26 October, and the missing VOCs data were replaced by the average value during the observation period. Only isoprene was considered in the BVOCs contribution.

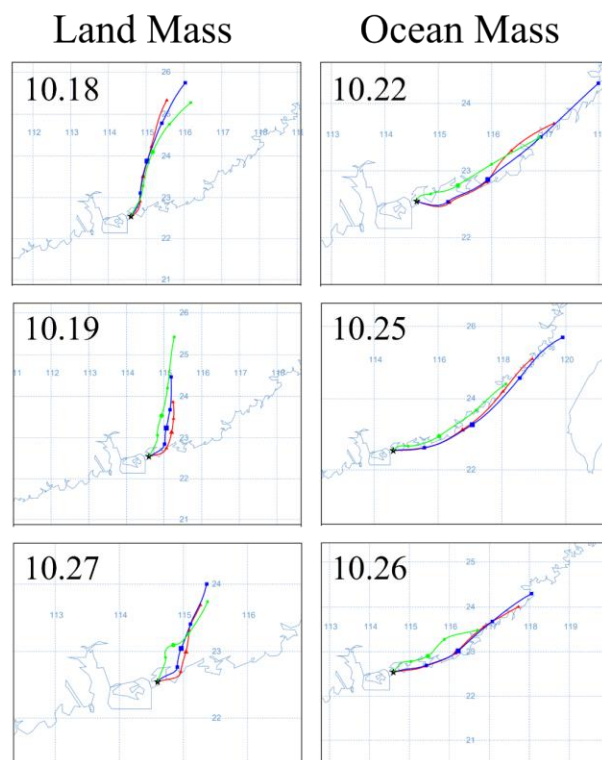


Fig. S2. The 24-h backward trajectories calculated at an arrival time of 12:00 (local time) at 100, 500, 1000 m above ground level at YMK in special days;

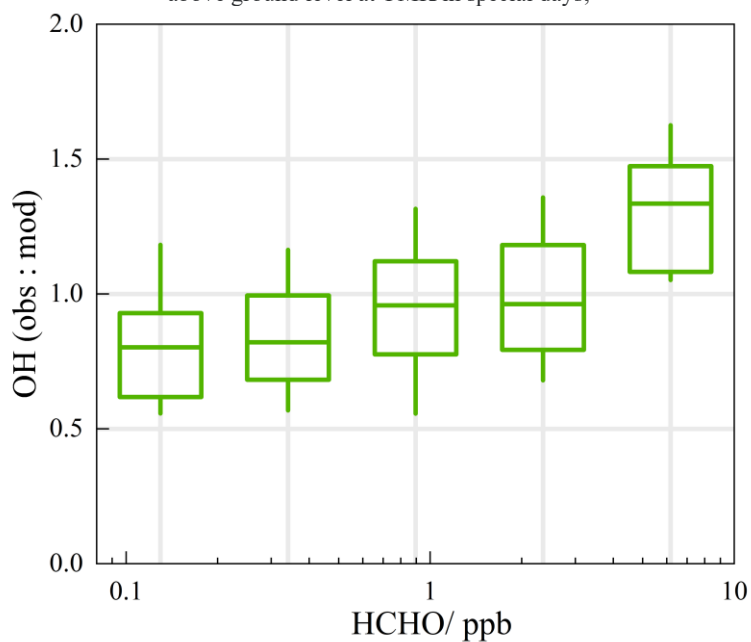


Fig. S3. The Obs-to-Mod ratio of OH radical as a function of HCHO in diurnal time. Daytime data are restricted according to $j(\text{O}^1\text{D}) > 0.5 \times 10^{-5} \text{ s}^{-1}$. Boxplot gives the minimum, 25%, median, 75%, and maximum of the data.