

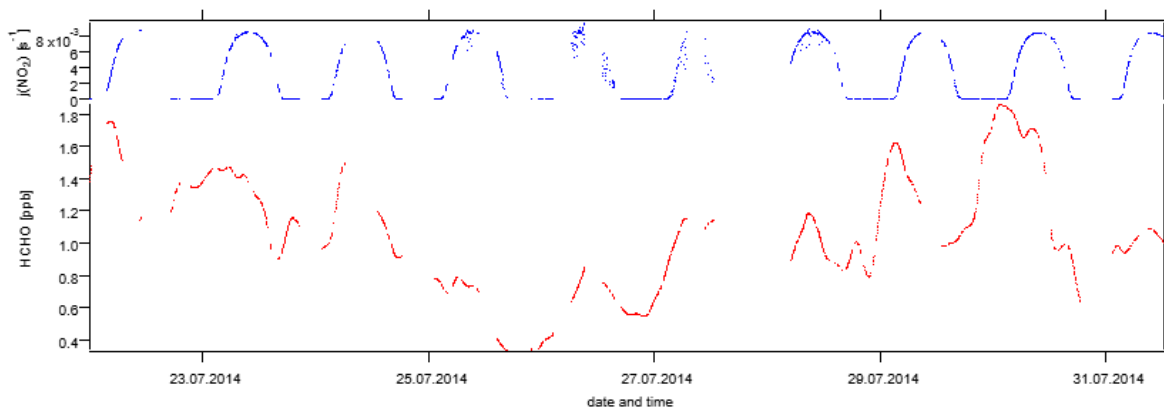
Table S1. Overview of applied rate constants.

rate constant	value / calculation [$\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$]
$k_{\text{CH}_4+\text{OH}}^1$	$1.85 \times 10^{-12} \times \exp(-1690 \text{ K}/T)$
$k_{\text{CH}_3\text{CHO}+\text{OH}}^1$	$4.7 \times 10^{-12} \times \exp(345 \text{ K}/T)$
$k_{\text{CH}_3\text{OH}+\text{OH}}^1$	$2.85 \times 10^{-12} \times \exp(-345 \text{ K}/T)$
$k_{\text{CH}_3\text{O}_2+\text{NO}}^1$	$2.3 \times 10^{-12} \times \exp(360 \text{ K}/T)$
$k_{\text{CH}_3\text{O}_2+\text{HO}_2}^1$	$3.8 \times 10^{-13} \times \exp(780 \text{ K}/T)$
$k_{\text{CH}_3\text{O}_2+\text{OH}}^1$	$3.7 \times 10^{-11} \times \exp(350 \text{ K}/T)$
$k_{\text{C}_5\text{H}_8(\text{OH})\text{O}_2+\text{NO}}^2$	9.0×10^{-12}
$k_{\text{C}_5\text{H}_8(\text{OH})\text{O}_2+\text{HO}_2}^2$	1.3×10^{-11}
$k_{\text{C}_5\text{H}_8(\text{OH})\text{O}_2+\text{RO}_2}^2$	6.6×10^{-14}
$k_{\text{C}_5\text{H}_8+\text{OH}}^1$	$2.1 \times 10^{-11} \times \exp(465 \text{ K}/T)$
$k_{\text{C}_5\text{H}_8+\text{O}_3}^1$	$1.05 \times 10^{-14} \times \exp(-2000 \text{ K}/T)$
$k_{\text{C}_2\text{H}_4+\text{O}_3}^1$	$6.82 \times 10^{-15} \times \exp(-2500 \text{ K}/T)$
$k_{\text{CH}_3\text{OOH}+\text{OH}}^1$	$5.3 \times 10^{-12} \times \exp(190 \text{ K}/T)$
$k_{\text{DMS}+\text{OH}}^3$	$1.13 \times 10^{-11} \times \exp(-253 \text{ K}/T) + \frac{1.0 \times 10^{-39} \times [\text{O}_2] \times \exp(5820 \text{ K}/T)}{1 + 5.0 \times 10^{-30} \times [\text{O}_2] \times \exp(6280 \text{ K}/T)}$
$k_{\text{HCHO}+\text{OH}}^1$	$5.4 \times 10^{-12} \times \exp(135 \text{ K}/T)$
$k_{\text{O}_3+\text{NO}}^1$	$2.07 \times 10^{-12} \times \exp(-1400 \text{ K}/T)$
$k_{\text{O}_3+\text{OH}}^4$	$1.7 \times 10^{-12} \times \exp(-940 \text{ K}/T)$
$k_{\text{O}_3+\text{HO}_2}^3$	$2.03 \times 10^{-16} \times (T/400 \text{ K})^{4.57} \times \exp(693 \text{ K}/T)$
$k_{\text{O}^1\text{D}+\text{O}_2}^1$	$3.2 \times 10^{-11} \times \exp(67 \text{ K}/T)$
$k_{\text{O}^1\text{D}+\text{N}_2}^1$	$2.15 \times 10^{-11} \times \exp(110 \text{ K}/T)$
$k_{\text{O}^1\text{D}+\text{H}_2\text{O}}^1$	2.14×10^{-10}

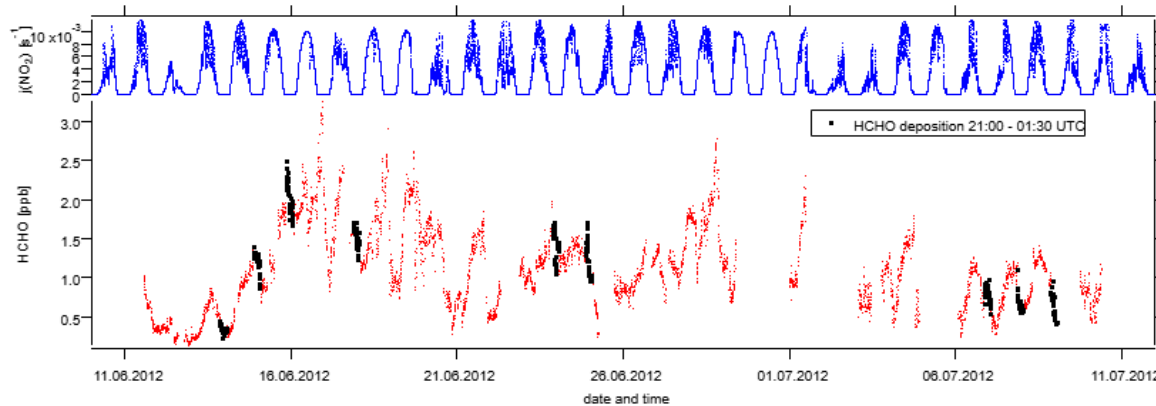
¹ IUPAC Task Group; ² Sumner et al., 2001; ³ Atkinson et al., 2004; ⁴ Atkinson et al., 2006;

Table S2. Total uncertainties and time resolution of the data used in this study.

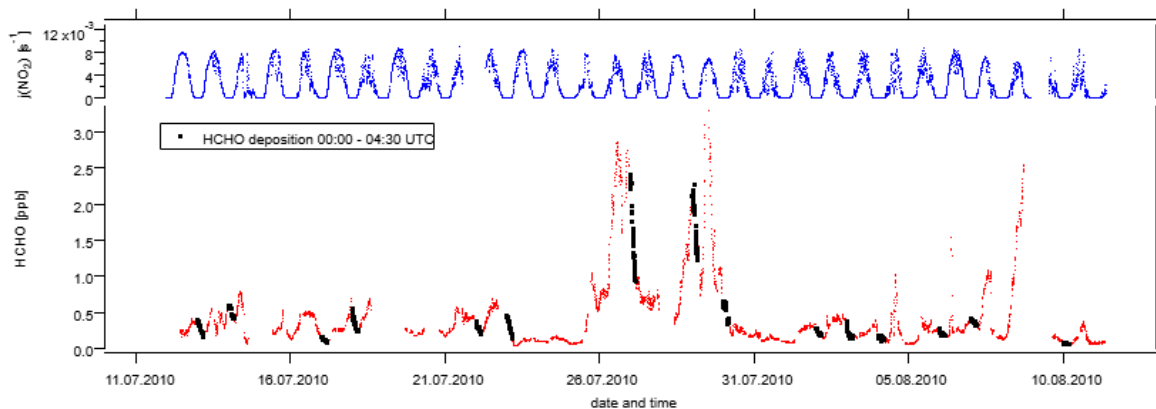
trace gas	total uncertainty [%]			time resolution [min]		
	CYPHEX	HOPE	HUMPPA	CYPHEX	HOPE	HUMPPA
NO	20	10	5	4	1	5
NO ₂	30	10	6	4	1	5
O ₃	5	5	10	4	1	5
HCHO	16	16	34	4	5	5
CH ₄	2	5	5	4	1	5
OH	28.5	30	30	4	5	10
HO ₂	36	40	40	4	5	10
C ₂ H ₄	10	-	-	4	-	-
C ₅ H ₈	14.5	15	15	4	1-4h	5
CH ₃ OH	41	14	20	4	1.5-3h	2h
CH ₃ CHO	27	13	20	4	1.5-3h	30
CH ₃ COCH ₃	17	-	-	4	-	-
DMS	17	-	-	1	-	-
CH ₃ OOH	9	-	-	4	-	-
j(O ¹ D)	10	10	10	10	1	30
j(NO ₂)	10	10	10	10	1	5
j(HCHO)	20	20	20	10	1	5
j(CH ₃ CHO)	20	-	-	10	-	-
j(CH ₃ COCH ₃)	20	-	-	10	-	-
j(CH ₃ OOH)	20	-	-	10	-	-
BLH	-	20	20	-	-	-
v_d	-	58	43	-	-	-



(a) CYPHEX 2014



(b) HOPE 2012



(c) HUMPPA 2010

Figure S1. Temporal development of the HCHO concentration and the NO₂ photolysis frequency during each research campaign. For HOPE and HUMPPA, these plots can be used for determining the HCHO deposition velocity at nighttime.

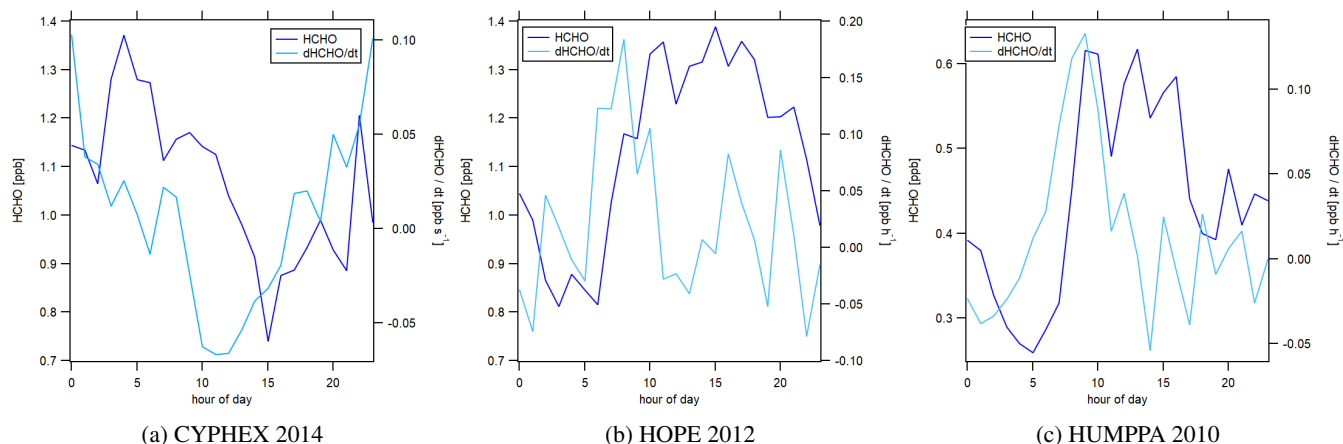


Figure S2. Diurnal average of HCHO concentrations including the rate of change $d\text{HCHO}/dt$.

Table S3. Calculated uncertainties resulting from the measurement uncertainties (MU) and from the atmospheric variability (AV). All uncertainties were calculated via Gaussian error propagation. For CYPHEX, AV1 relates to the point-by-point calculation and AV2 relates to preaveraging and subsequent diurnal calculations. All values are in %. For the atmospheric variability, the number in brackets refers to the all-day average and the number without brackets refers to the daytime average. α_1 is $\alpha_{\text{CH}_3\text{O}_2}$ and α_2 is $\alpha_{\text{CH}_3\text{CHO}}$.

term	calculation	CYPHEX			HOPE		HUMPPA	
		MU	AV1	AV2	MU	AV	MU	AV
HCHO								
P(CH ₄ +OH)	$k \times [\text{CH}_4] \times [\text{OH}] \times \alpha_1$	29	37 (61)	33 (54)	30	52 (62)	30	49 (49)
P(CH ₃ CHO+OH)	$k \times [\text{CH}_3\text{CHO}] \times [\text{OH}] \times \alpha_1 \times \alpha_2$	39	57 (79)	50 (67)	33	75 (80)	36	71 (71)
P(CH ₃ OH+OH)	$k \times [\text{CH}_3\text{OH}] \times [\text{OH}]$	50	41 (60)	39 (59)	33	65 (74)	36	85 (81)
P(C ₅ H ₈ +OH)	$k \times [\text{C}_5\text{H}_8] \times [\text{OH}] \times \text{yield}$	32	56 (71)	54 (71)	34	92 (96)	34	96 (104)
P(HCHO) _{basic}	$\sum P_n$ (basic)	31	40 (61)	22 (34)	31	42 (46)	31	38 (39)
P(HCHO) _{all}	$\sum P_n$ (all)	28	38 (58)	-	-	-	-	-
L(HCHO+OH)	$k \times [\text{HCHO}] \times [\text{OH}]$	33	44 (64)	42 (62)	34	65 (76)	45	113 (118)
L(HCHO+hν)	$j(\text{HCHO}) \times [\text{HCHO}]$	26	32 (-)	31 (-)	26	59 (-)	39	111 (-)
L(HCHO) deposition	$[\text{HCHO}] \times \frac{v_d}{BLH}$	-	-	-	63	72 (75)	58	75 (83)
L(HCHO)	$\sum L_n$	26	34 (57)	25 (52)	34	43 (50)	44	78 (87)
O₃								
P(NO ₂ +hν)	$j(\text{NO}_2) \times [\text{NO}_2]$	32	68 (-)	66 (-)	14	58 (-)	12	44 (-)
P(O ₃)	P(NO ₂ +hν)	32	68 (-)	66 (-)	14	58 (-)	12	44 (-)
L(O ₃ +NO)	$k \times [\text{O}_3] \times [\text{NO}]$	21	46 (51)	42 (55)	11	97 (119)	11	63 (93)
L(O ₃ +hν)	$j(\text{O}^1\text{D}) \times [\text{O}_3] \times \alpha$	11	32 (-)	30 (-)	11	71 (-)	14	50 (-)
L(O ₃ +OH)	$k \times [\text{O}_3] \times [\text{OH}]$	29	37 (58)	35 (57)	30	58 (66)	32	53 (54)
L(O ₃ +HO ₂)	$k \times [\text{O}_3] \times [\text{HO}_2]$	36	27 (41)	23 (35)	40	57 (55)	41	42 (56)
L(O ₃) deposition	$[\text{O}_3] \times \frac{v_d}{BLH}$	-	-	-	21	24 (24)	22	21 (23)
L(O ₃)	$\sum L_n$	16	37 (44)	34 (49)	10	83 (94)	13	51 (49)

Uncertainty Calculations: We exemplarily present the calculation of the uncertainties of P_{CH_4+OH} in Equations (S1)-(S4) and of $P(HCHO)_{basic}$ in Equations (S5)-(S7) according to gaussian error propagation. All other calculations are accordingly.

Example 1:

$$P_{CH_4+OH} = k_{CH_4+OH} \times [CH_4] \times [OH] \times \alpha_{CH_3O_2} \quad (S1)$$

$$\begin{aligned} \Delta P_{CH_4+OH}^2 &= \left(\frac{dP(CH_4+OH)}{d[CH_4]} \right)^2 \times \Delta[CH_4]^2 + \left(\frac{dP(CH_4+OH)}{d[OH]} \right)^2 \times \Delta[OH]^2 \\ &= k_{CH_4+OH}^2 \times [CH_4]^2 \times \alpha_{CH_3O_2}^2 \times \Delta[OH]^2 + k_{CH_4+OH}^2 \times [OH]^2 \times \alpha_{CH_3O_2}^2 \times \Delta[CH_4]^2 \end{aligned} \quad (S2)$$

$$\begin{aligned} \frac{\Delta P_{CH_4+OH}^2}{P_{CH_4+OH}^2} &= \frac{k_{CH_4+OH}^2 \times [CH_4]^2 \times \alpha_{CH_3O_2}^2 \times \Delta[OH]^2 + k_{CH_4+OH}^2 \times [OH]^2 \times \alpha_{CH_3O_2}^2 \times \Delta[CH_4]^2}{k_{CH_4+OH}^2 \times [CH_4]^2 \times [OH]^2 \times \alpha_{CH_3O_2}^2} \\ &= \frac{[CH_4]^2 \times \Delta[OH]^2 + [OH]^2 \times \Delta[CH_4]^2}{[CH_4]^2 \times [OH]^2} \end{aligned} \quad (S3)$$

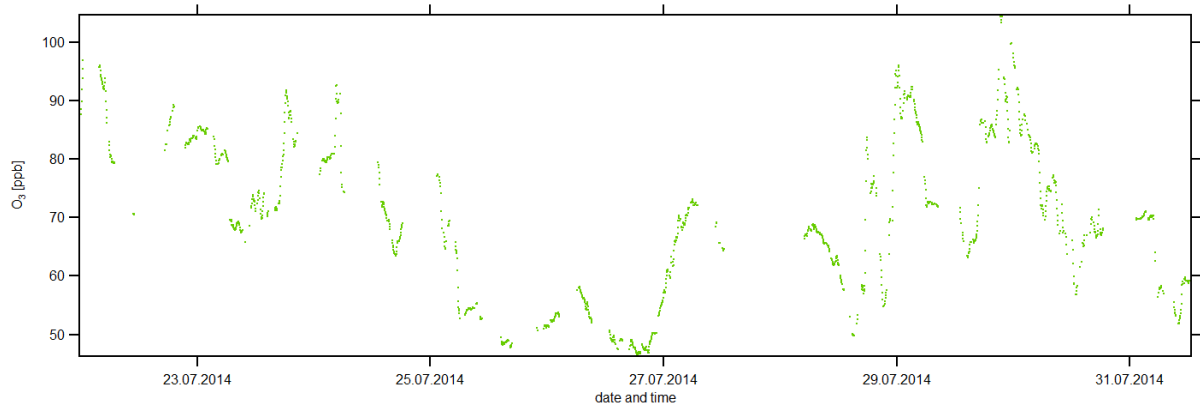
$$\frac{\Delta P_{CH_4+OH}}{P_{CH_4+OH}} = \sqrt{\frac{\Delta[OH]^2}{[OH]^2} + \frac{\Delta[CH_4]^2}{[CH_4]^2}} \quad (S4)$$

Example 2:

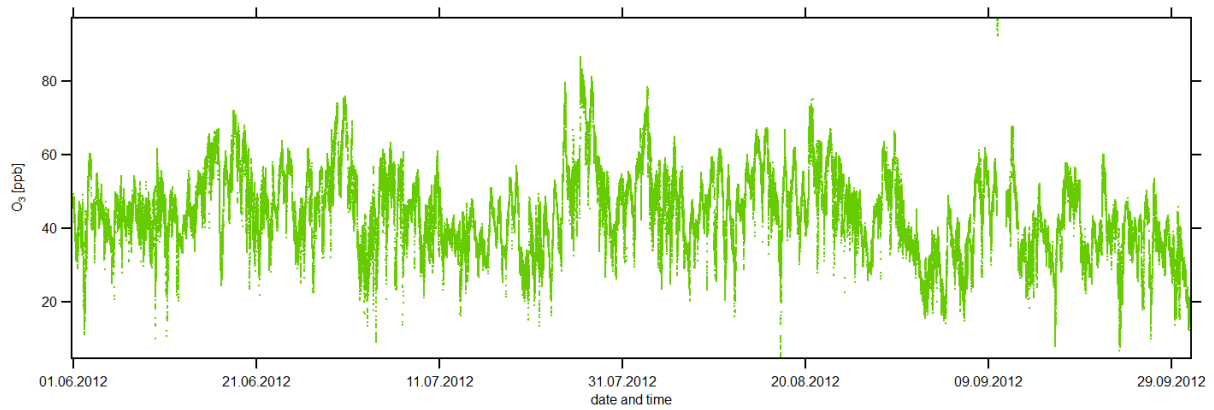
$$\begin{aligned} P(HCHO)_{basic} &= P_{CH_4+OH} + P_{CH_3CHO+OH} + P_{CH_3OH+OH} + P_{C_5H_8+OH} \\ &= [OH] \times ([CH_4] \times k_{CH_4+OH} \times \alpha_{CH_3O_2} + [CH_3CHO] \times k_{CH_3CHO+OH} \times \alpha_{CH_3O_2} \times \alpha_{CH_3CHO} \\ &\quad + [CH_3OH] \times k_{CH_3OH+OH} + [C_5H_8] \times k_{C_5H_8+OH} \times \alpha_{Isoprene}) \end{aligned} \quad (S5)$$

$$\begin{aligned} \Delta P(HCHO)_{basic}^2 &= \left(\frac{dP(HCHO)_{basic}}{d[OH]} \right)^2 \times \Delta[OH]^2 + \left(\frac{dP(HCHO)_{basic}}{d[CH_4]} \right)^2 \times \Delta[CH_4]^2 \\ &\quad + \left(\frac{dP(HCHO)_{basic}}{d[CH_3CHO]} \right)^2 \times \Delta[CH_3CHO]^2 + \left(\frac{dP(HCHO)_{basic}}{d[CH_3OH]} \right)^2 \times \Delta[CH_3OH]^2 \\ &\quad + \left(\frac{dP(HCHO)_{basic}}{d[C_5H_8]} \right)^2 \times \Delta[C_5H_8]^2 \\ &= ([CH_4] \times k_{CH_4+OH} \times \alpha_{CH_3O_2} + [CH_3CHO] \times k_{CH_3CHO+OH} \times \alpha_{CH_3O_2} \times \alpha_{CH_3CHO} \\ &\quad + [CH_3OH] \times k_{CH_3OH+OH} + [C_5H_8] \times k_{C_5H_8+OH} \times \alpha_{Isoprene})^2 \times \Delta[OH]^2 \\ &\quad + k_{CH_4+OH}^2 \times \alpha_{CH_3O_2}^2 \times [OH]^2 \times \Delta[CH_4]^2 + k_{CH_3CHO+OH}^2 \times \alpha_{CH_3O_2}^2 \times \alpha_{CH_3CHO}^2 \\ &\quad \times [OH]^2 \times \Delta[CH_3CHO]^2 + k_{CH_3OH+OH}^2 \times [OH]^2 \times \Delta[CH_3OH]^2 \\ &\quad + k_{C_5H_8+OH}^2 \times \alpha_{Isoprene}^2 \times [OH]^2 \times \Delta[C_5H_8]^2 \end{aligned} \quad (S6)$$

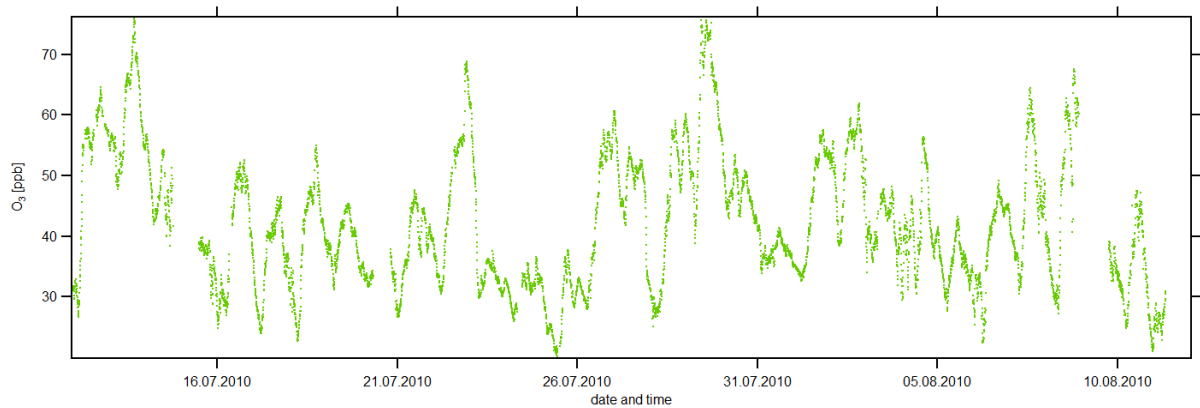
$$\begin{aligned}
\frac{\Delta P(HCHO)_{basic}}{P(HCHO)_{basic}} &= \sqrt{\frac{\Delta P(HCHO)_{basic}^2}{P(HCHO)_{basic}^2}} \\
&= \sqrt{\frac{([CH_4] \times k_{CH_4+OH} \times \alpha_{CH_3O_2} + [CH_3CHO] \times k_{CH_3CHO+OH} \times \alpha_{CH_3O_2} \times \alpha_{CH_3CHO} \\
&\quad + [CH_3OH] \times k_{CH_3OH+OH} + [C_5H_8] \times k_{C_5H_8+OH} \times \alpha_{Isoprene})^2 \times \Delta[OH]^2}{+ k_{CH_4+OH}^2 \times \alpha_{CH_3O_2}^2 \times [OH]^2 \times \Delta[CH_4]^2 + k_{CH_3CHO+OH}^2 \times \alpha_{CH_3O_2}^2 \times \alpha_{CH_3CHO}^2 \times [OH]^2 \\
&\quad \times \Delta[CH_3CHO]^2 + k_{CH_3OH+OH}^2 \times [OH]^2 \times \Delta[CH_3OH]^2 + k_{C_5H_8+OH}^2 \times \alpha_{Isoprene} \times [OH]^2)}{1}} \\
&\quad \times \Delta[C_5H_8]^2 \times \frac{1}{(P_{CH_4+OH} + P_{CH_3CHO+OH} + P_{CH_3OH+OH} + P_{C_5H_8+OH})^2}
\end{aligned} \tag{S7}$$



(a) CYPHEX 2014



(b) HOPE 2012



(c) HUMPPA 2010

Figure S3. Temporal development of the O_3 concentration in the scope of each research campaign.

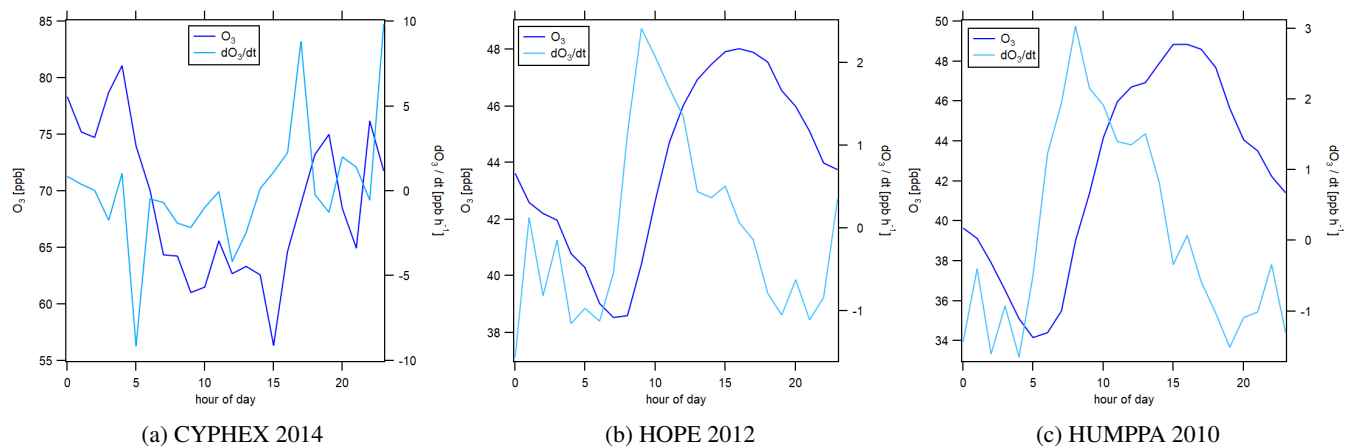
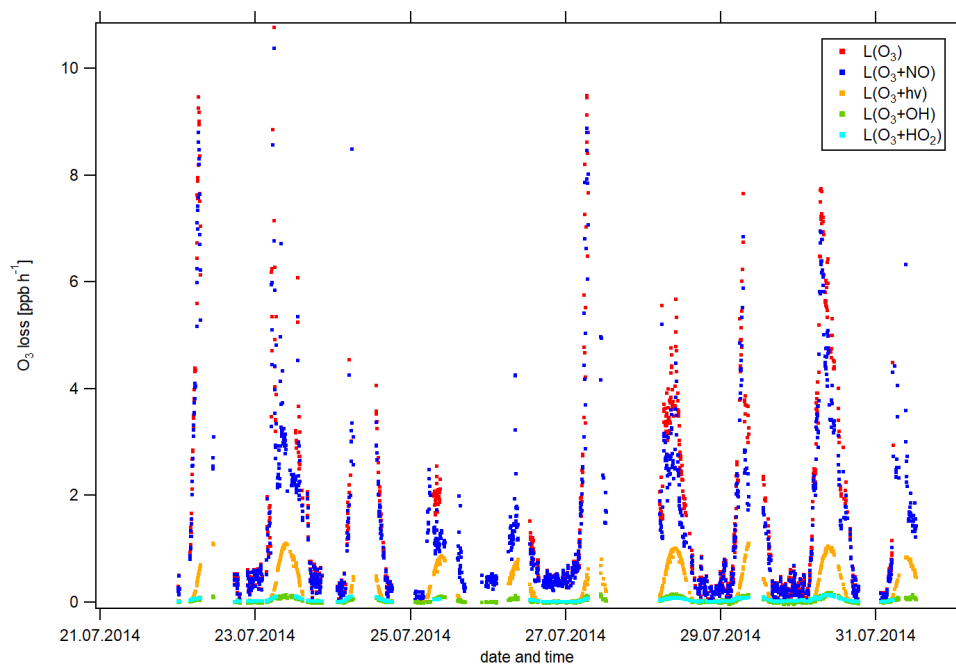
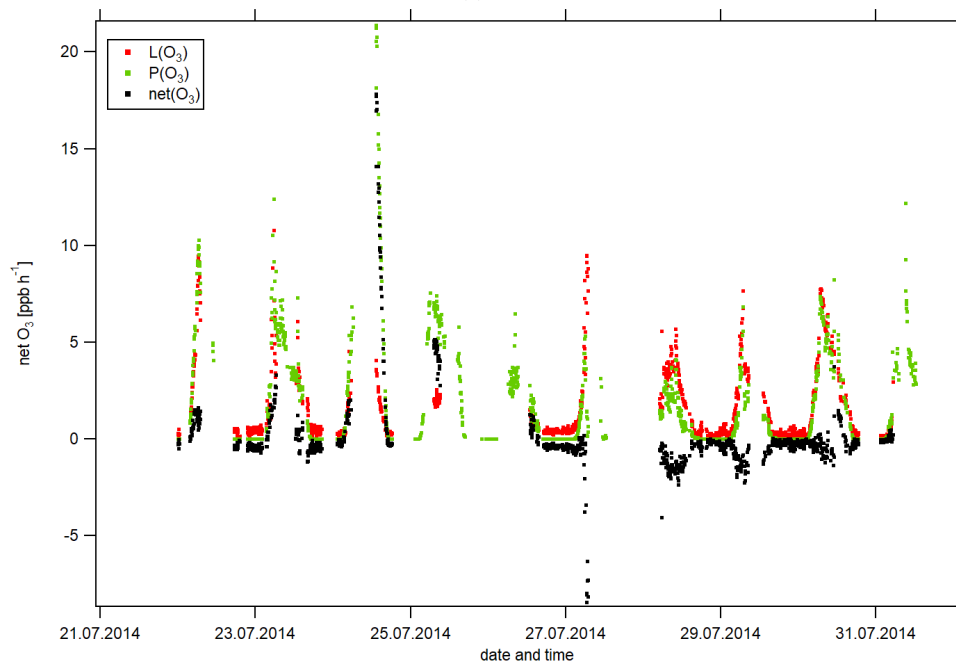


Figure S4. Diurnal average of O_3 concentrations including the rate of change dO_3/dt .



(a) O_3 loss



(b) net O_3 production

Figure S5. Temporal development of O_3 production and loss terms from July 22 to July 31, 2014 during the research campaign CYPHEX in Cyprus.

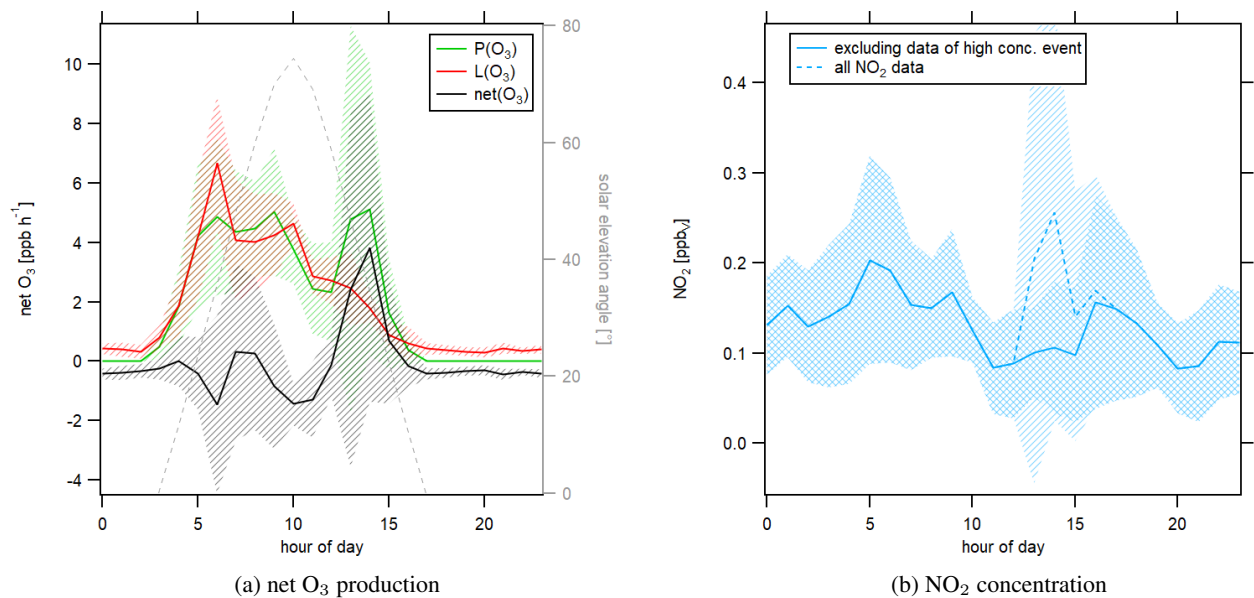


Figure S6. (a) Diurnal O₃ production and loss during CYPHEX, including all data points. (b) Diurnal NO₂ concentrations with and without afternoon peak caused by a singular high concentration event on July 24 (13:15 - 16:15 UTC).

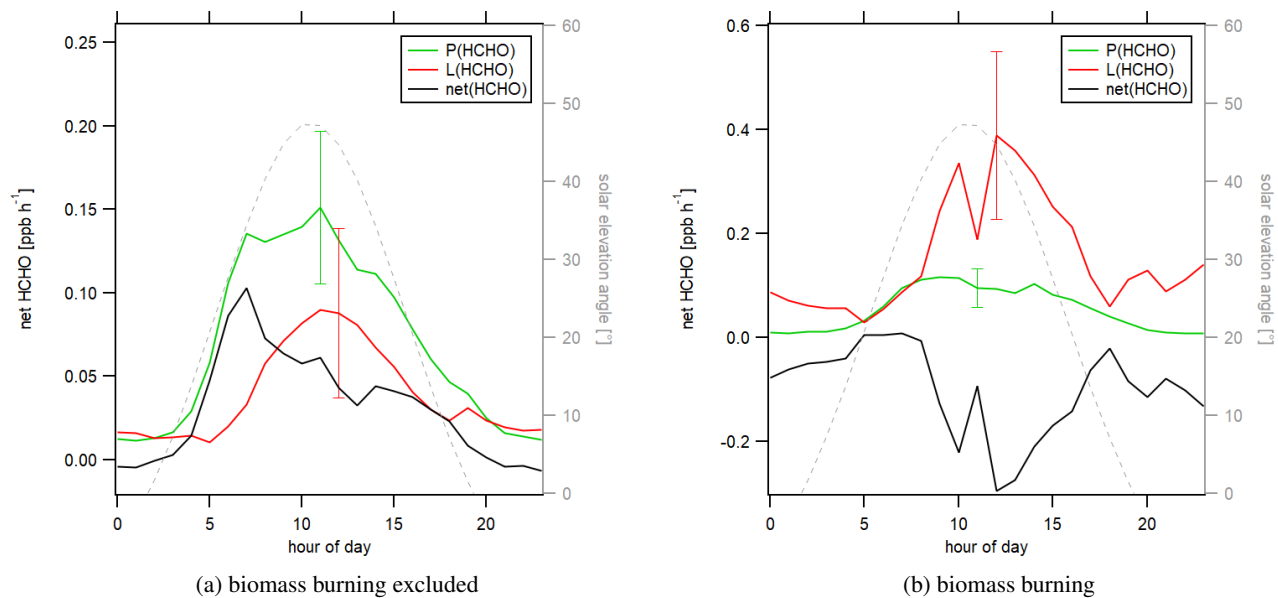


Figure S7. Diurnal HCHO production and loss during CYPHEX (a) considering only data which were impacted by biomass burning (BB) and (b) excluding data with BB impact.