Supplement of Atmos. Chem. Phys., 21, 18413–18432, 2021
https://doi.org/10.5194/acp-21-18413-2021-supplement

Atmospheric Chemistry and Physics
Open Access

Supplement of

Measurement report: Photochemical production and loss rates of formaldehyde and ozone across Europe

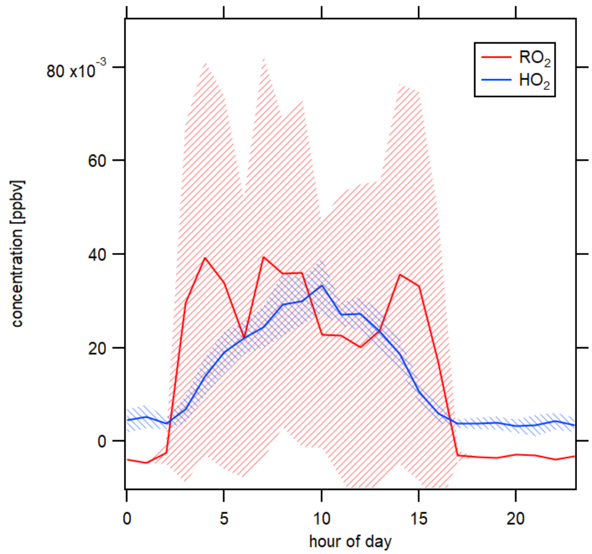
Clara M. Nussbaumer et al.

Correspondence to: Clara M. Nussbaumer (clara.nussbaumer@mpic.de)

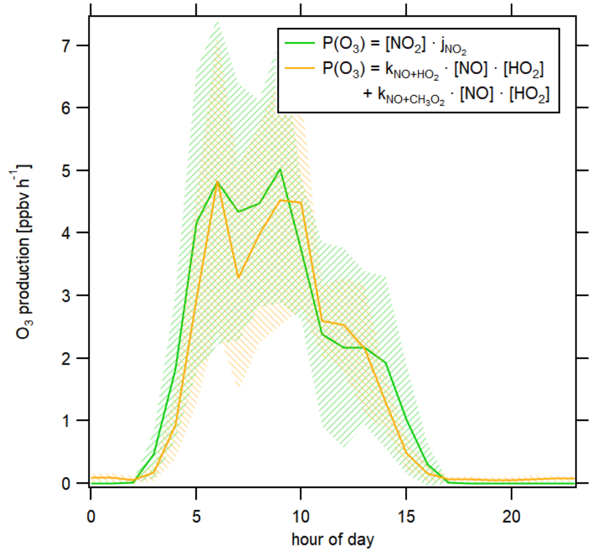
Table S1. Overview of applied rate constants.

rate constant	value / calculation [cm^3 molecule^{-1} s^{-1}]
k_{CH_4+OH} [1]	$1.85 \times 10^{-12} \times exp(-1690\,\mathrm{K}/T)$
$k_{CH_3CHO+OH}$ [1]	$4.7 \times 10^{-12} \times exp(345\,\mathrm{K}/T)$
k_{CH_3OH+OH} [1]	$2.85 \times 10^{-12} \times exp(-345\,\mathrm{K}/T)$
$k_{CH_3O_2+NO}$ [1]	$2.3 \times 10^{-12} \times exp(360\,\mathrm{K}/T)$
$k_{CH_3O_2+HO_2}$ [1]	$3.8 \times 10^{-13} \times exp(780\,\mathrm{K}/T)$
$k_{CH_3O_2+OH}$ [1]	$3.7 \times 10^{-11} \times exp(350\,\mathrm{K}/T)$
$k_{C_5H_8(OH)O_2+NO}$ [2]	9.0×10^{-12}
$k_{C_5H_8(OH)O_2+HO_2}$ [2]	1.3×10^{-11}
$k_{C_5H_8(OH)O_2+RO_2}$ [2]	6.6×10^{-14}
$k_{C_5H_8+OH}$ [1]	$2.1 \times 10^{-11} \times exp(465\,\mathrm{K}/T)$
$k_{C_5H_8+O_3}$ [1]	$1.05 \times 10^{-14} \times exp(-2000\,\mathrm{K}/T)$
$k_{C_2H_4+O_3}$ [1]	$6.82 \times 10^{-15} \times exp(-2500\,\mathrm{K}/T)$
$k_{CH_3OOH+OH}$ [1]	$5.3 \times 10^{-12} \times exp(190\,\mathrm{K}/T)$
k_{DMS+OH} [3]	$1.13 \times 10^{-11} \times exp(-253\,\mathrm{K}/T) + \frac{1.0 \times 10^{-39} \times [O_2] \times exp(5820\,\mathrm{K}/T)}{1 + 5.0 \times 10^{-30} \times [O_2] \times exp(6280\,\mathrm{K}/T)}$
$k_{HCHO+OH}$ [1]	$5.4 \times 10^{-12} \times exp(135\,\mathrm{K}/T)$
k_{O_3+NO} [1]	$2.07 \times 10^{-12} \times exp(-1400\,\mathrm{K}/T)$
k_{O_3+OH} [4]	$1.7 \times 10^{-12} \times exp(-940\,\mathrm{K}/T)$
$k_{O_3+HO_2}$ [3]	$2.03 \times 10^{-16} \times (T/400\,\mathrm{K})^{4.57} \times exp(693\,\mathrm{K}/T)$
$k_{O^1D+O_2}$ [1]	$3.2 \times 10^{-11} \times exp(67\,\mathrm{K}/T)$
$k_{O^1D+N_2}$ [1]	$2.15 \times 10^{-11} \times exp(110\,\mathrm{K}/T)$
$k_{O^1D+H_2O}$ [1]	2.14×10^{-10}

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



(a) HO_2 and RO_2



(b) $P(O_3)$

Figure S1. (a) Diurnal profile of HO_2 and calculated RO_2 during CYPHEX through equating $P(O_3)$ from NO_2 photolysis and $P(O_3)$ from reaction of NO with HO_2 and RO_2 (b) O_3 production calculated via the photolytic reaction of NO_2, and the reaction of HO_2 and RO_2 with NO, assuming $[HO_2]=[RO_2]$. We use the rate constant $k_{NO+CH_3O_2}$ as surrogate for k_{NO+RO_2}. Both panels show close agreement which justifies the assumption that $[HO_2]=[RO_2]$.

Table S2. Coefficients for the calculation of j(HCHO) and j(CH_3CHO) according to Equation (S1).

species	a_1	a_2 [s]	b_1	b_2 [s]
HCHO	1.719	-1.768×10^{4}	4.701×10^{-3}	-3.471×10^{-2}
CH_3CHO	1.516×10^{-1}	-8.970×10^{2}	4.567×10^{-5}	1.711×10^{-3}

$$j(species)_{parameter} = a_1 \times j(O^1D) + a_2 \times (j(O^1D))^2 + b_1 \times j(NO_2) + b_2 \times (j(NO_2))^2 \tag{S1}$$

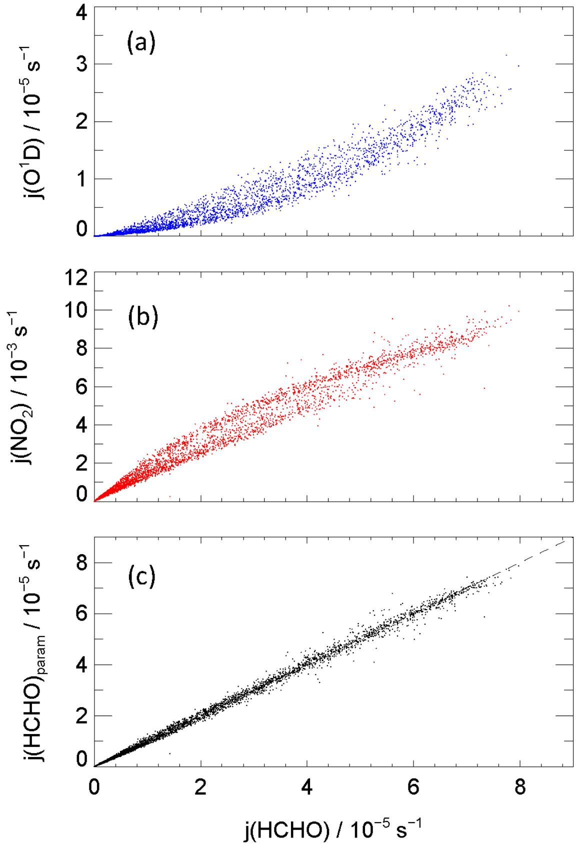
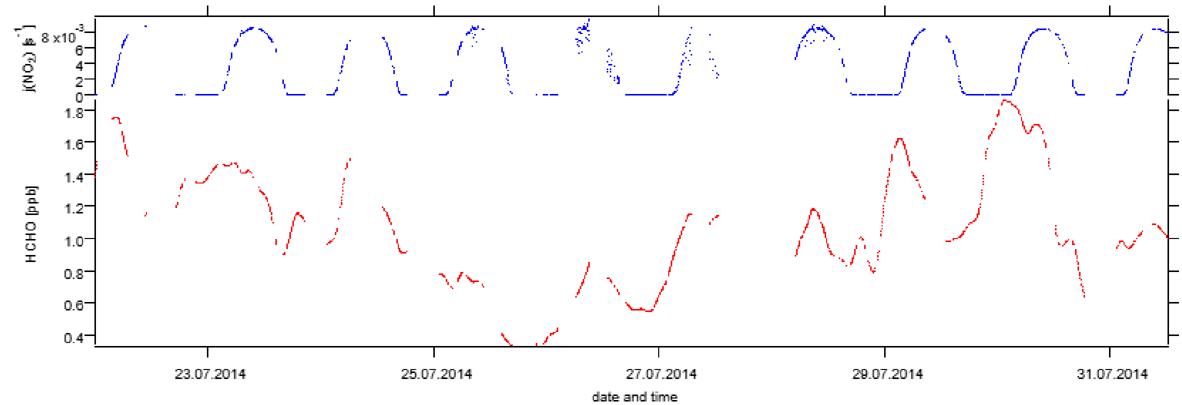


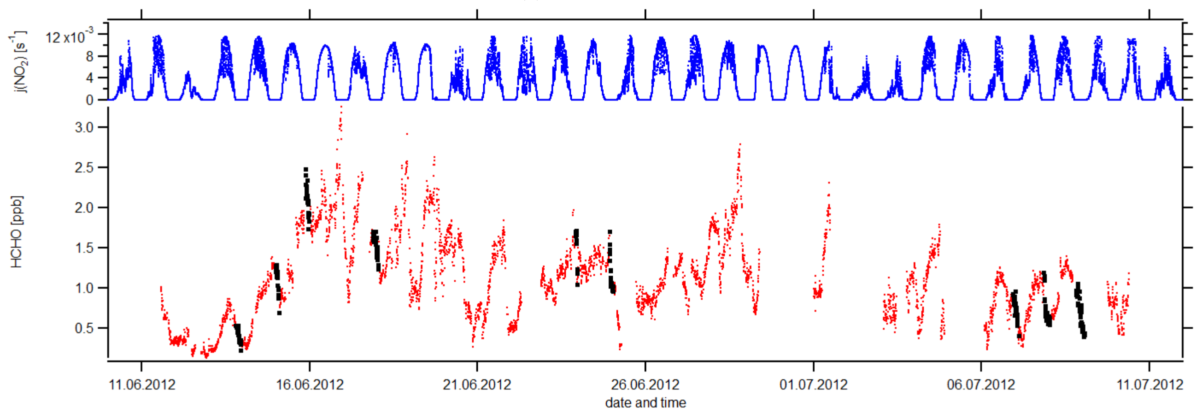
Figure S2. Correlations of measured j(HCHO) (molecular plus radical channel) with (a) j(O_1D) and (b) j(NO_2) from spectroradiometer measurements. The correlation of measured and parameterized j(HCHO) according to Equation (S1) is shown in panel (c). Only one out of ten data points from the original data set is shown for clarity.

Table S3. Total uncertainties and time resolution of the data used in this study.

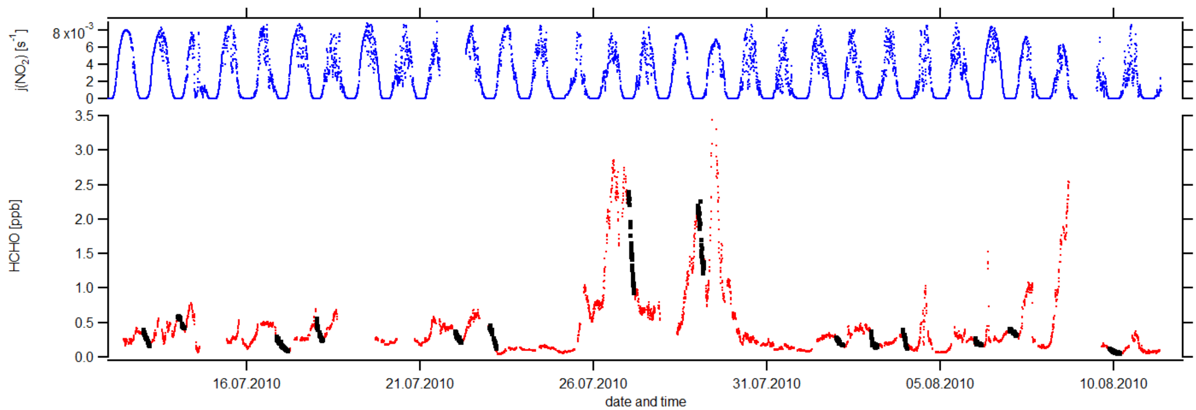
	total uncertainty [%]			time resolution [min]		
trace gas	CYPHEX	HOPE	HUMPPA	CYPHEX	HOPE	HUMPPA
NO	20	10	5	5s	1	5
NO_2	30	10	6	5s	1	5
O_3	5	5	10	1	1	5
HCHO	16	16	34	10	5	5
CH_4	2	5	5	1	1	5
OH	28.5	30	30	4	5	10
HO_2	36	40	40	14s	5	10
C_2H_4	10	-	-	1h	-	-
C_5H_8	14.5	15	15	45	1-4h	5
CH_3OH	41	14	20	1	1.5-3h	2h
CH_3CHO	27	13	20	1	1.5-3h	30
CH_3COCH_3	17	-	-	1	-	-
DMS	17	-	-	1	-	-
CH_3OOH	9	-	-	12	-	-
j(O^1D)	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_3CHO)	20	-	-	10	-	-
j(CH_3COCH_3)	20	-	-	10	-	-
j(CH_3OOH)	20	-	-	10	-	-
BLH	-	20	20	-	-	-
v_d	-	54	54	-	-	-



(a) CYPHEX 2014

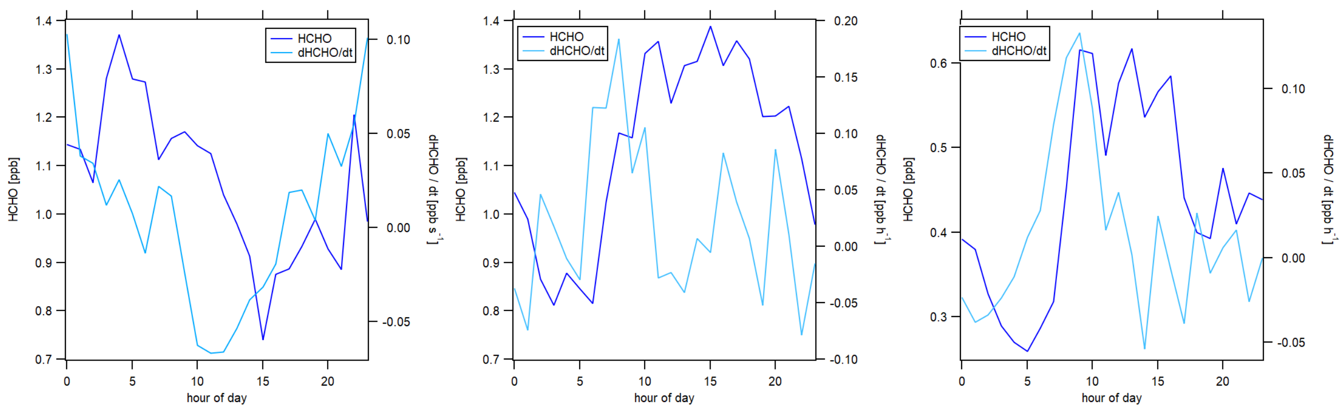


(b) HOPE 2012



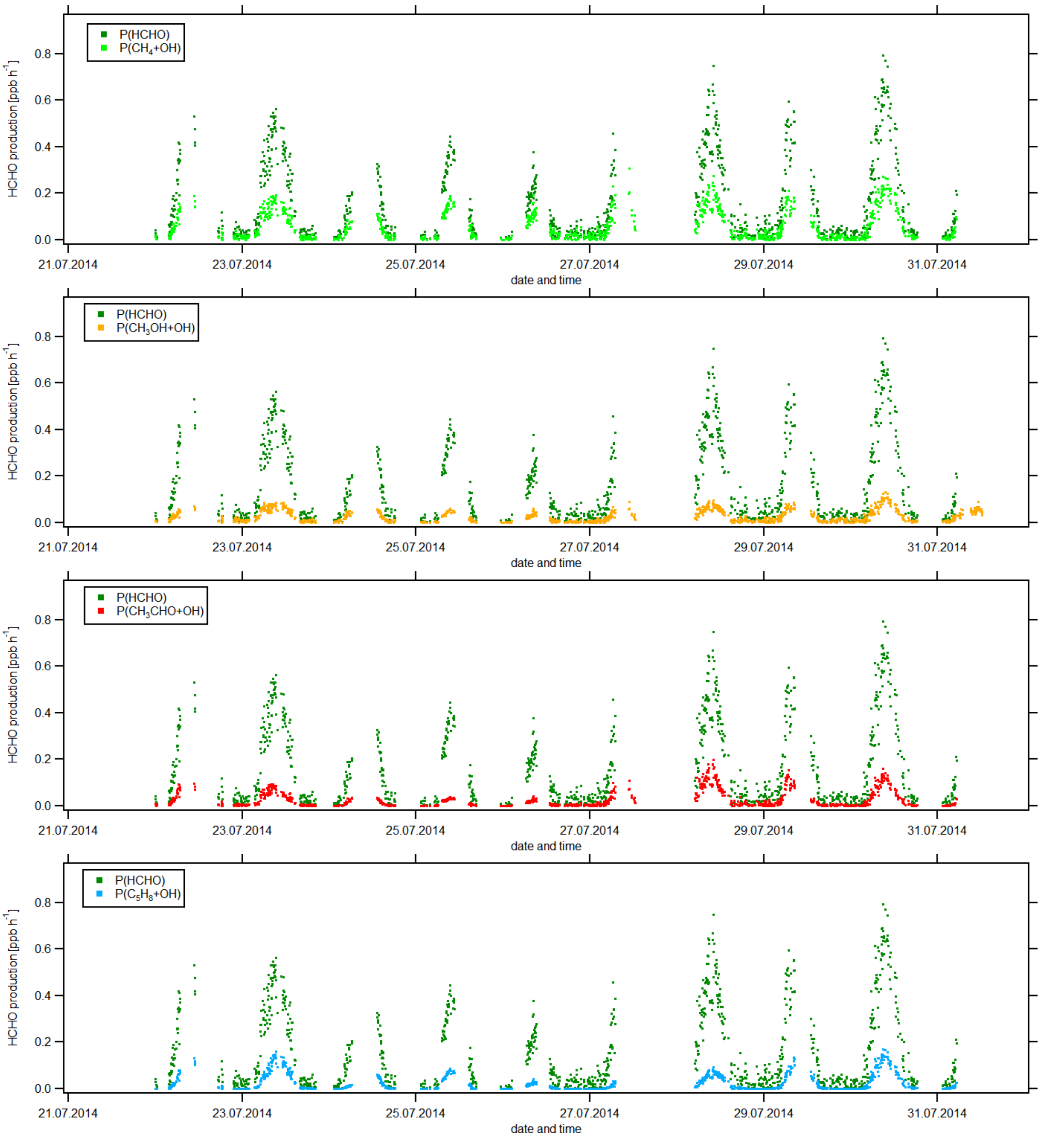
(c) HUMPPA 2010

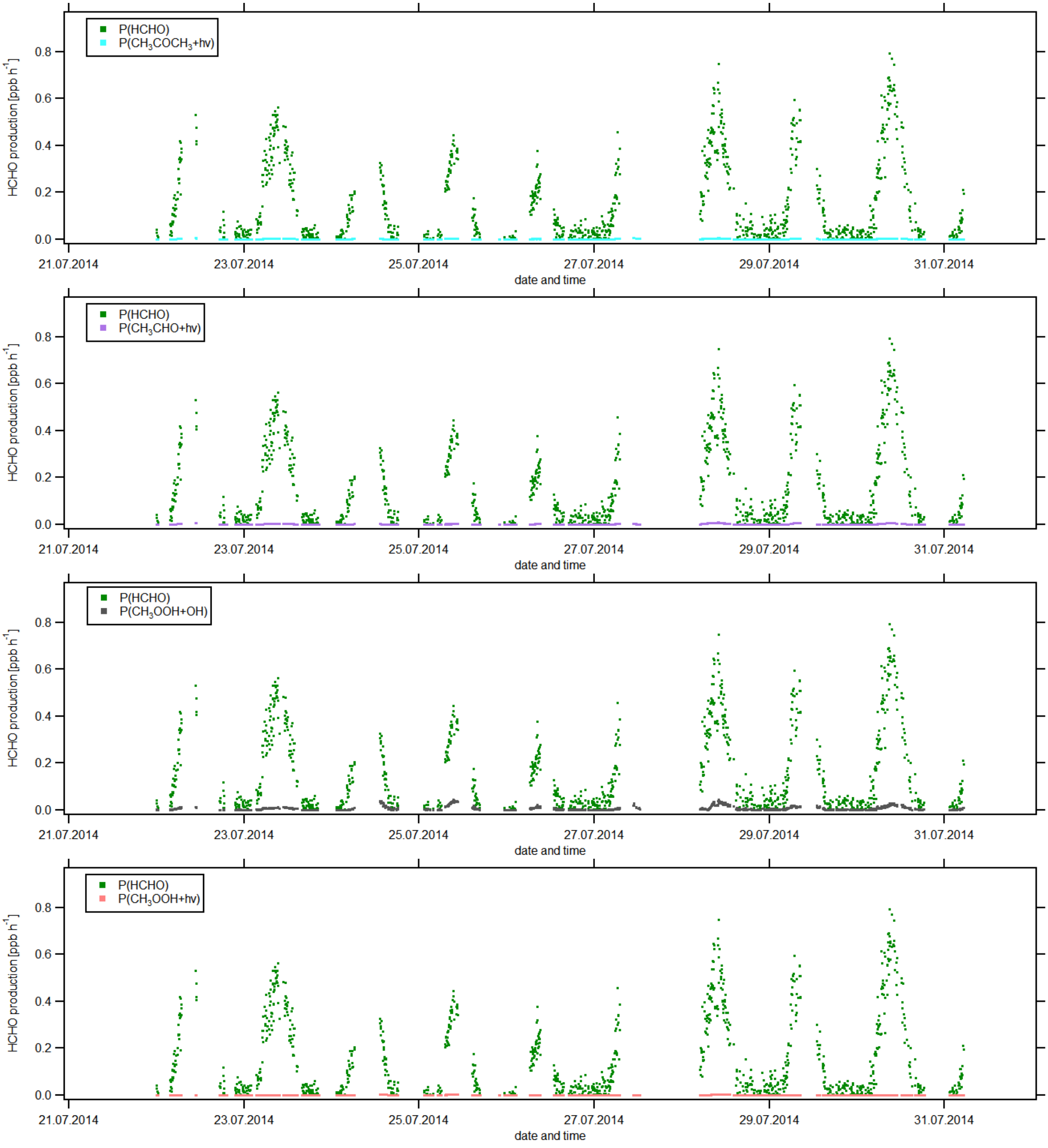
Figure S3. Temporal development of the HCHO concentration and the NO_2 photolysis frequency during each research campaign. For HOPE and HUMPPA, these plots can be used for determining the HCHO deposition velocity at nighttime.



(a) CYPHEX 2014 (b) HOPE 2012 (c) HUMPPA 2010

Figure S4. Diurnal average of HCHO concentrations including the rate of change dHCHO/dt.


P(HCHO)
P(CH$_4$+OH)
HCHO production [ppb h^{-1}]
0.0
0.2
0.4
0.6
0.8
21.07.2014
23.07.2014
25.07.2014
27.07.2014
29.07.2014
31.07.2014
date and time
P(HCHO)
P(CH$_3$OH+OH)
P(HCHO)
P(CH$_3$CHO+OH)
P(HCHO)
P(C$_5$H$_8$+OH)


P(HCHO)
P(CH3COCH3+hv)
P(CH3CHO+hv)
P(CH3OOH+OH)
P(CH3OOH+hv)
HCHO production [ppb h-1]
0.0
0.2
0.4
0.6
0.8
21.07.2014
23.07.2014
25.07.2014
27.07.2014
29.07.2014
31.07.2014
date and time

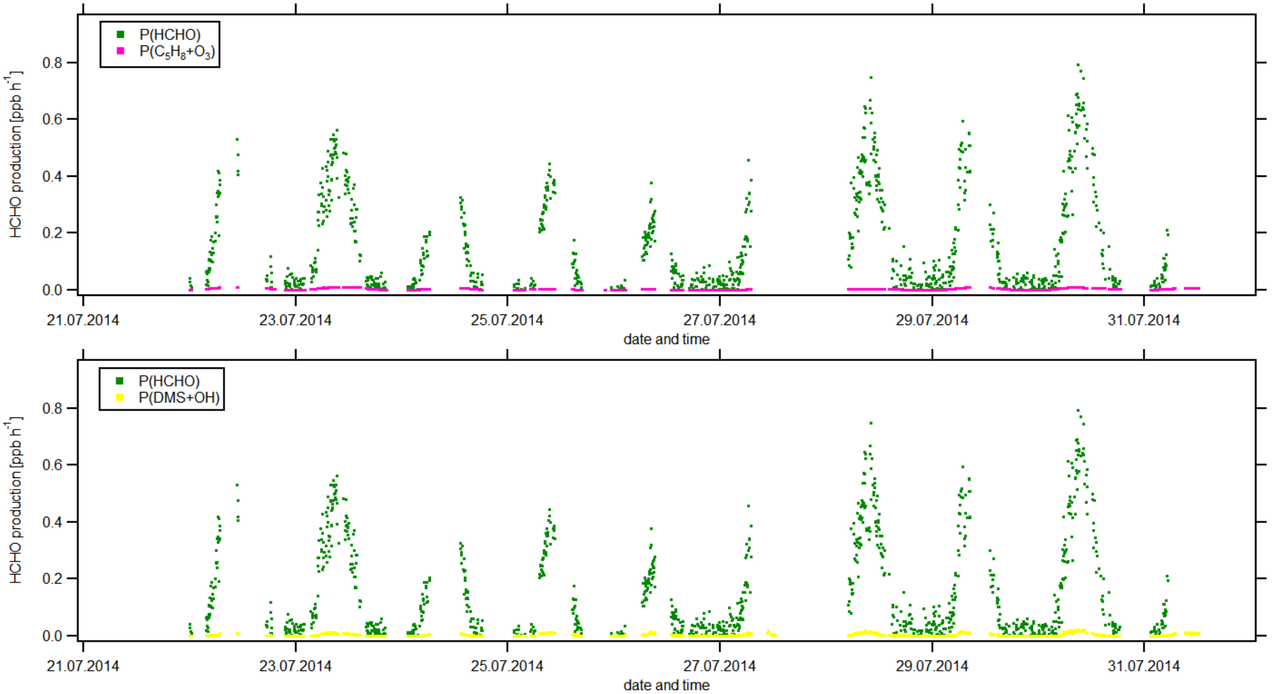


Figure S5. Individual panels of all HCHO production terms.

Table S4. 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 $\alpha_{CH_3O_2}$ and α_2 is α_{CH_3CHO}.

		CYPHEX			HOPE		HUMPPA	
term	calculation	MU	AV1	AV2	MU	AV	MU	AV
HCHO								
P(CH_4+OH)	k×[CH_4]×[OH]×α_1	29	37 (61)	33 (54)	30	52 (62)	30	49 (49)
P(CH_3CHO+OH)	k×[CH_3CHO]×[OH]×$\alpha_1 \times \alpha_2$	39	57 (79)	50 (67)	33	75 (80)	36	71 (71)
P(CH_3OH+OH)	k×[CH_3OH]×[OH]	50	41 (60)	39 (59)	33	65 (74)	36	85 (81)
P(C_5H_8+OH)	k×[C_5H_8]×[OH]× yield	32	55 (71)	54 (71)	34	92 (96)	34	96 (104)
P(HCHO)$_{basic}$	$\sum$ P_n (basic)	31	40 (61)	22 (34)	31	42 (45)	31	38 (39)
P(HCHO)$_{all}$	$\sum$ P_n (all)	28	38 (58)	-	-	-	-	-
L(HCHO+OH)	k×[HCHO]×[OH]	33	44 (64)	42 (62)	34	65 (76)	45	113 (118)
L(HCHO+hν)	j(HCHO)×[HCHO]	26	32 (-)	31 (-)	26	59 (-)	39	111 (-)
L(HCHO) deposition	[HCHO]×$\frac{v_d}{BLH}$	-	-	-	63	69 (73)	58	112 (117)
L(HCHO)	$\sum$ L_n	26	34 (57)	25 (52)	34	40 (51)	44	77 (87)
O_3								
P(NO_2+hν)	j(NO_2)×[NO_2]	32	59 (-)	57 (-)	14	58 (-)	12	44 (-)
P(O_3)	P(NO_2+hν)	32	59 (-)	57 (-)	14	58 (-)	12	44 (-)
L(O_3+NO)	k×[O_3]×[NO]	21	46 (51)	42 (55)	11	97 (119)	11	63 (93)
L(O_3+hν)	j(O^1D)×[O_3]×α	11	32 (-)	30 (-)	11	71 (-)	14	50 (-)
L(O_3+OH)	k×[O_3]×[OH]	29	37 (58)	35 (57)	30	58 (66)	32	53 (54)
L(O_3+HO_2)	k×[O_3]×[HO_2]	36	27 (41)	23 (35)	40	57 (55)	41	42 (56)
L(O_3) deposition	[O_3]×$\frac{v_d}{BLH}$	-	-	-	21	24 (24)	22	21 (23)
L(O_3)	$\sum$ L_n	16	37 (44)	35 (49)	10	90 (98)	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:

$$P_{CH_4+OH} = k_{CH_4+OH} \times [CH_4] \times [OH] \times \alpha_{CH_3O_2} \tag{S2}$$

$$\begin{aligned}\Delta P^2_{CH_4+OH} &= \left(\frac{dP(CH_4+OH)}{d[CH_4]}\right)^2 \times \Delta[CH_4]^2 + \left(\frac{dP(CH_4+OH)}{d[OH]}\right)^2 \times \Delta[OH]^2 \\ &= k^2_{CH_4+OH} \times [CH_4]^2 \times \alpha^2_{CH_3O_2} \times \Delta[OH]^2 + k^2_{CH_4+OH} \times [OH]^2 \times \alpha^2_{CH_3O_2} \times \Delta[CH_4]^2\end{aligned} \tag{S3}$$

$$\begin{aligned}\frac{\Delta P^2_{CH_4+OH}}{P^2_{CH_4+OH}} &= \frac{k^2_{CH_4+OH} \times [CH_4]^2 \times \alpha^2_{CH_3O_2} \times \Delta[OH]^2 + k^2_{CH_4+OH} \times [OH]^2 \times \alpha^2_{CH_3O_2} \times \Delta[CH_4]^2}{k^2_{CH_4+OH} \times [CH_4]^2 \times [OH]^2 \times \alpha^2_{CH_3O_2}} \\ &= \frac{[CH_4]^2 \times \Delta[OH]^2 + [OH]^2 \times \Delta[CH_4]^2}{[CH_4]^2 \times [OH]^2}\end{aligned} \tag{S4}$$

$$\frac{\Delta P_{CH_4+OH}}{P_{CH_4+OH}} = \sqrt{\frac{\Delta[OH]^2}{[OH]^2} + \frac{\Delta[CH_4]^2}{[CH_4]^2}} \tag{S5}$$

Example 2:

$$\begin{aligned}P(HCHO)_{basic} &= P_{CH_4+OH} + P_{CH_3CHO+OH} + P_{CH_3OH+OH} + P_{C_5H_8+OH} \\ &= [OH] \times ([CH_4] \times k_{CH_4+OH} \times \alpha_{CH_3O_2} + [CH_3CHO] \times k_{CH_3CHO+OH} \times \alpha_{CH_3O_2} \times \alpha_{CH_3CHO} \\ &+ [CH_3OH] \times k_{CH_3OH+OH} + [C_5H_8] \times k_{C_5H_8+OH} \times \alpha_{Isoprene})\end{aligned} \tag{S6}$$

$$\begin{aligned}\Delta P(HCHO)^2_{basic} &= \left(\frac{dP(HCHO)_{basic}}{d[OH]}\right)^2 \times \Delta[OH]^2 + \left(\frac{dP(HCHO)_{basic}}{d[CH_4]}\right)^2 \times \Delta[CH_4]^2 \\ &+ \left(\frac{dP(HCHO)_{basic}}{d[CH_3CHO]}\right)^2 \times \Delta[CH_3CHO]^2 + \left(\frac{dP(HCHO)_{basic}}{d[CH_3OH]}\right)^2 \times \Delta[CH_3OH]^2 \\ &+ \left(\frac{dP(HCHO)_{basic}}{d[C_5H_8]}\right)^2 \times \Delta[C_5H_8]^2 \\ &= ([CH_4] \times k_{CH_4+OH} \times \alpha_{CH_3O_2} + [CH_3CHO] \times k_{CH_3CHO+OH} \times \alpha_{CH_3O_2} \times \alpha_{CH_3CHO} \\ &+ [CH_3OH] \times k_{CH_3OH+OH} + [C_5H_8] \times k_{C_5H_8+OH} \times \alpha_{Isoprene})^2 \times \Delta[OH]^2 \\ &+ k^2_{CH_4+OH} \times \alpha^2_{CH_3O_2} \times [OH]^2 \times \Delta[CH_4]^2 + k^2_{CH_3CHO+OH} \times \alpha^2_{CH_3O_2} \times \alpha^2_{CH_3CHO} \\ &\times [OH]^2 \times \Delta[CH_3CHO]^2 + k^2_{CH_3OH+OH} \times [OH]^2 \times \Delta[CH_3OH]^2 \\ &+ k^2_{C_5H_8+OH} \times \alpha_{Isoprene} \times [OH]^2 \times \Delta[C_5H_8]^2\end{aligned} \tag{S7}$$

$$\frac{\Delta P(HCHO)_{basic}}{P(HCHO)_{basic}} = \sqrt{\frac{\Delta P(HCHO)_{basic}^2}{P(HCHO)_{basic}^2}}$$

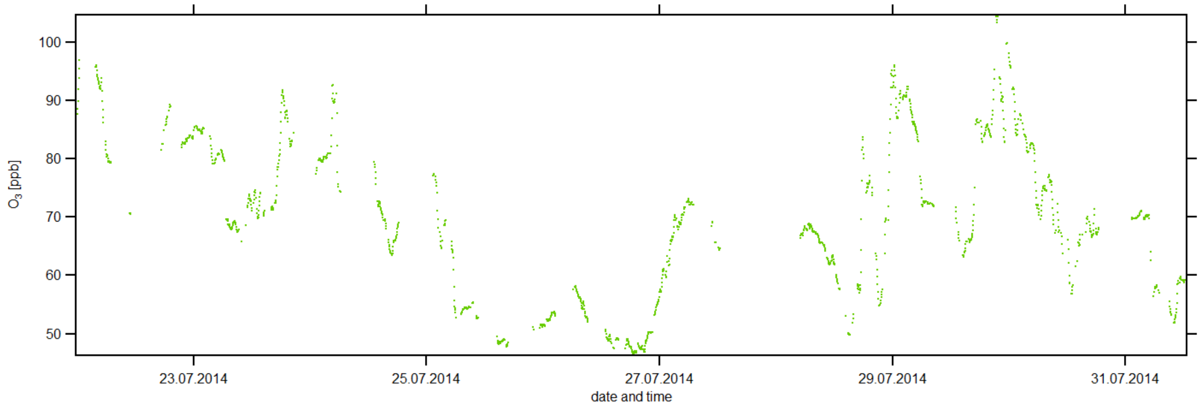
$$= \sqrt{(([CH_4] \times k_{CH_4+OH} \times \alpha_{CH_3O_2} + [CH_3CHO] \times k_{CH_3CHO+OH} \times \alpha_{CH_3O_2} \times \alpha_{CH_3CHO}}$$

$$\overline{+[CH_3OH] \times k_{CH_3OH+OH} + [C_5H_8] \times k_{C_5H_8+OH} \times \alpha_{Isoprene})^2 \times \Delta[OH]^2}$$

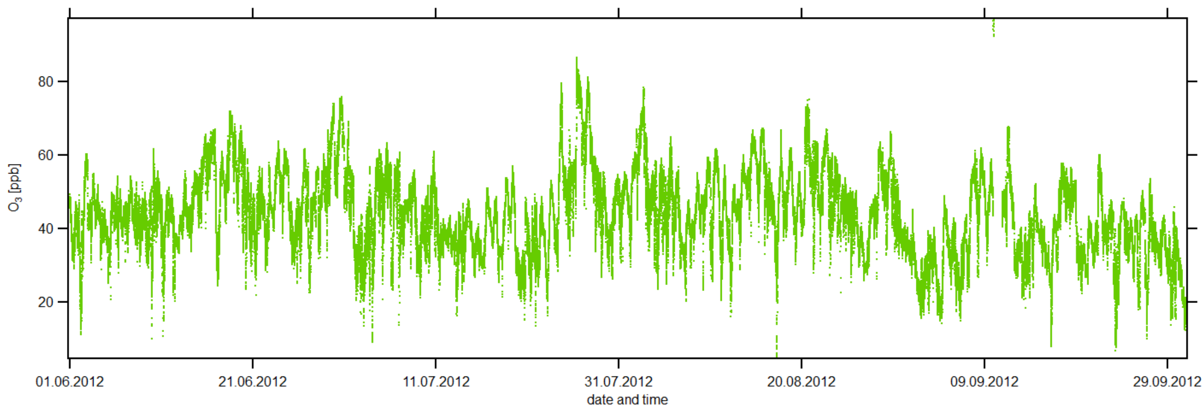
$$\overline{+k_{CH_4+OH}^2 \times \alpha_{CH_3O_2}^2 \times [OH]^2 \times \Delta[CH_4]^2 + k_{CH_3CHO+OH}^2 \times \alpha_{CH_3O_2}^2 \times \alpha_{CH_3CHO}^2 \times [OH]^2}$$

$$\overline{\times \Delta[CH_3CHO]^2 + k_{CH_3OH+OH}^2 \times [OH]^2 \times \Delta[CH_3OH]^2 + k_{C_5H_8+OH}^2 \times \alpha_{Isoprene} \times [OH]^2)}$$

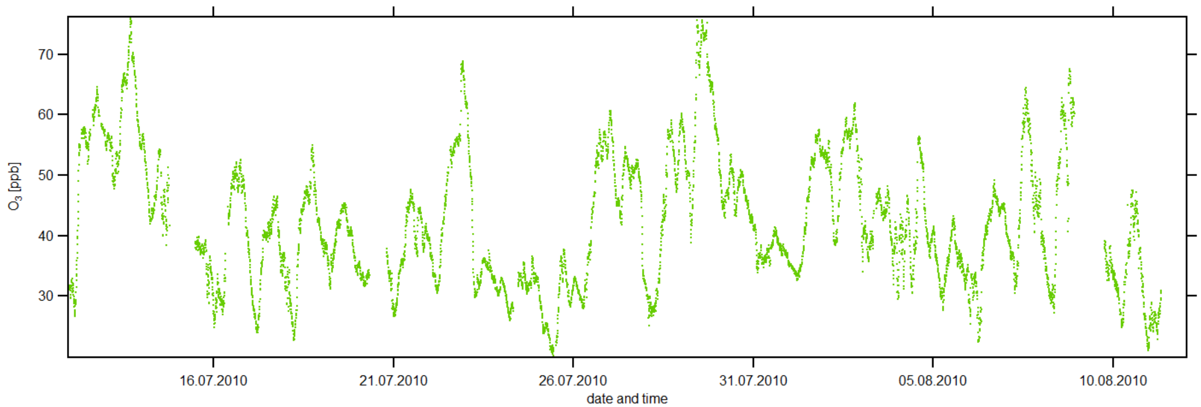
$$\overline{\times \Delta[C_5H_8]^2 \times \frac{1}{(P_{CH_4+OH} + P_{CH_3CHO+OH} + P_{CH_3OH+OH} + P_{C_5H_8+OH})^2}} \tag{S8}$$



(a) CYPHEX 2014

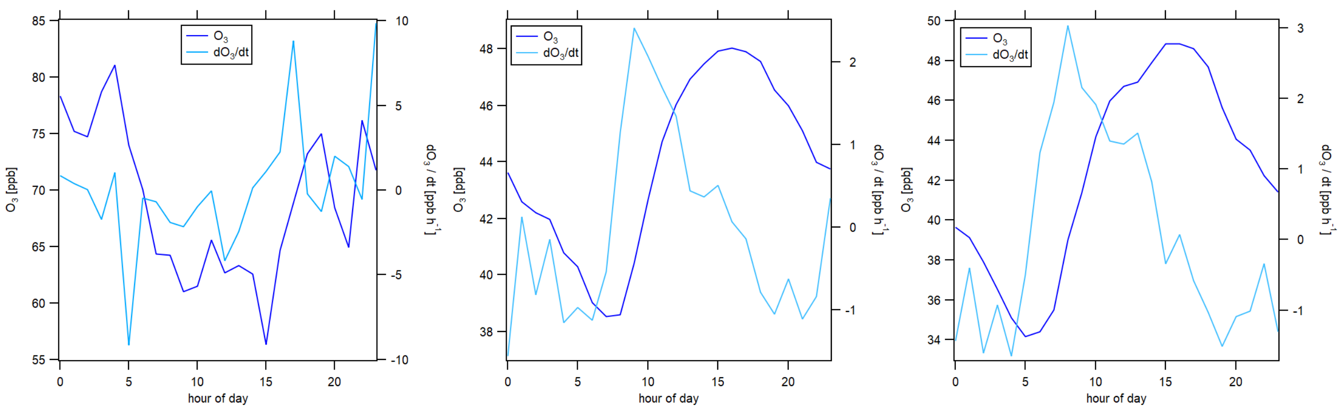


(b) HOPE 2012



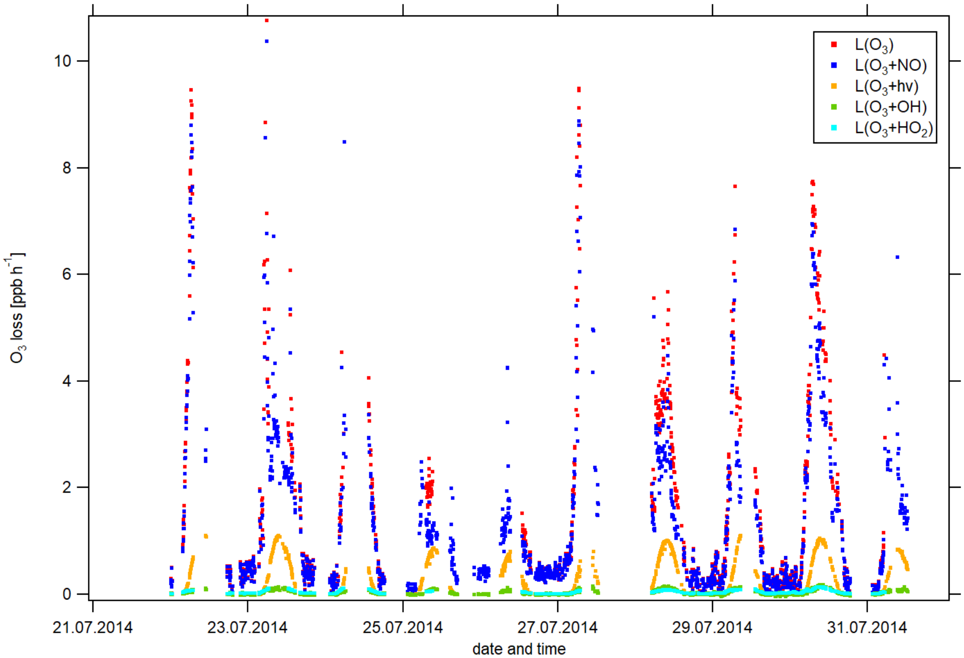
(c) HUMPPA 2010

Figure S6. Temporal development of the O_3 concentration in the scope of each research campaign.

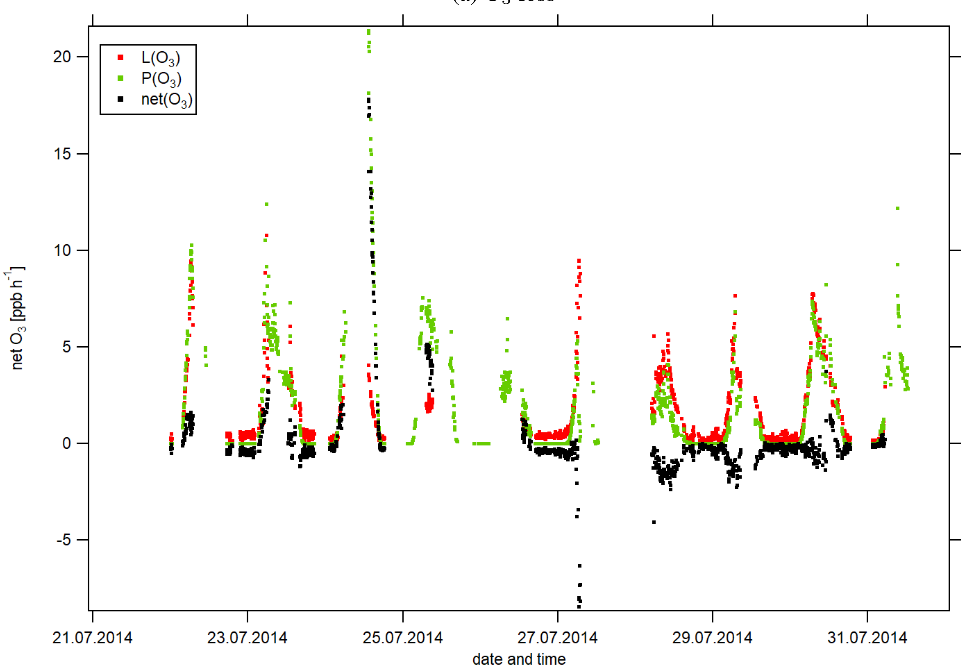


(a) CYPHEX 2014 (b) HOPE 2012 (c) HUMPPA 2010

Figure S7. Diurnal average of O_3 concentrations including the rate of change dO_3/dt.

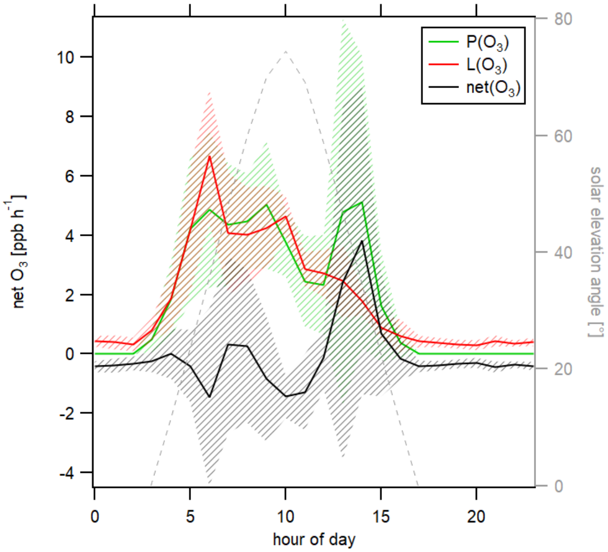


(a) O_3 loss

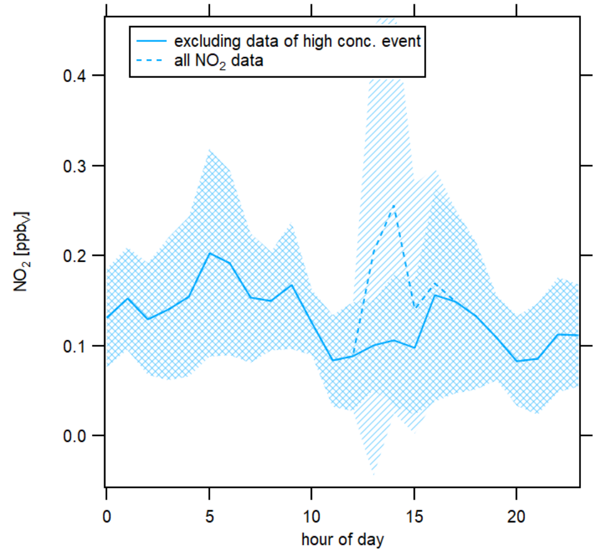


(b) net O_3 production

Figure S8. Temporal development of O_3 production and loss terms from July 22 to July 31, 2014 during the research campaign CYPHEX in Cyprus.

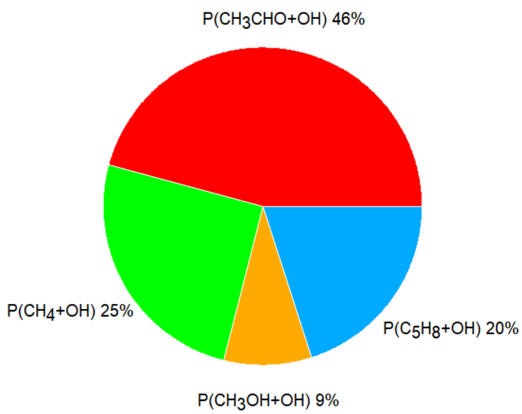


(a) net O_3 production

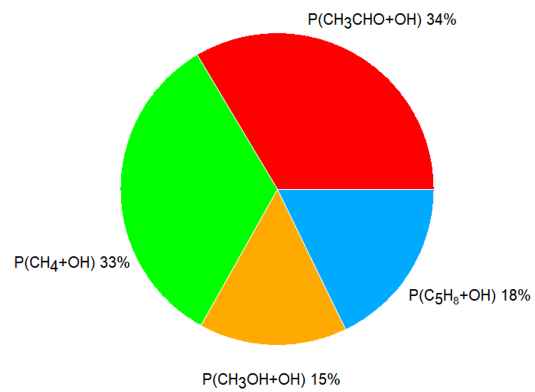


(b) NO_2 concentration

Figure S9. (a) Diurnal O_3 production and loss during CYPHEX, including all data points. (b) Diurnal NO_2 concentrations with and without afternoon peak caused by a singular high concentration event on July 24 (13:15 - 16.15 UTC).

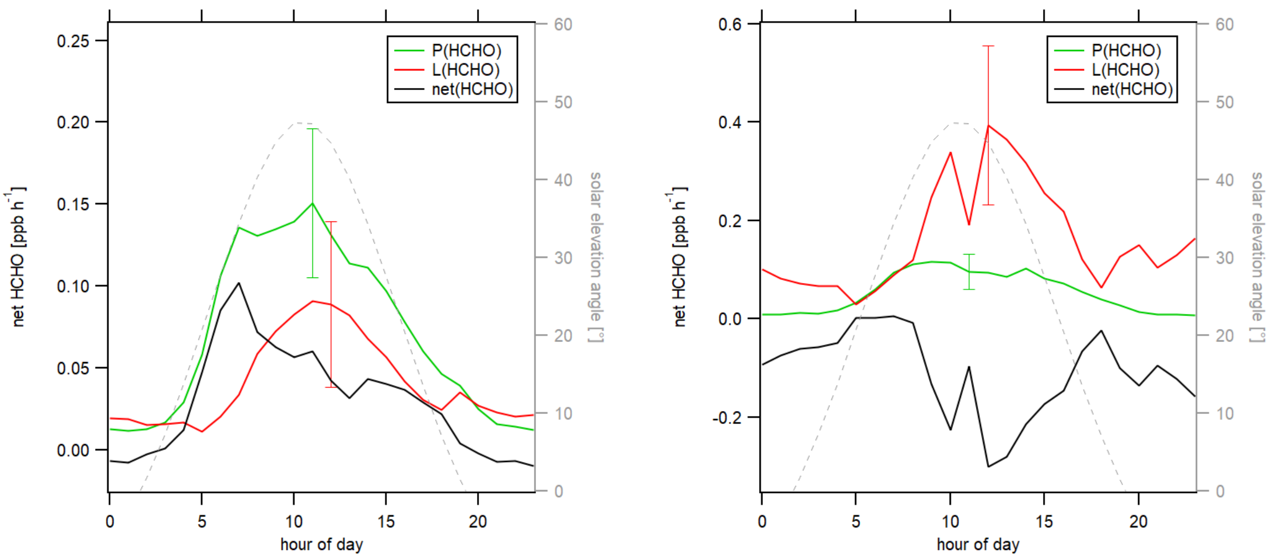


(a) HOPE



(b) HUMPPA

Figure S10. Chemical production terms of HCHO during (a) HOPE and (b) HUMPPA.



(a) biomass burning excluded

(b) biomass burning

Figure S11. Diurnal HCHO production and loss during HUMPPA (a) considering only data which were impacted by biomass burning (BB) and (b) excluding data with BB impact.