Supplementary Material of O_3-NO_y photochemistry in boundary layer polluted plumes: insights from the MEGAPOLI (Paris), ChArMEx/SAFMED (North West Mediterranean) and DACCIWA (southern West Africa) aircraft campaigns

B. Thera et al.

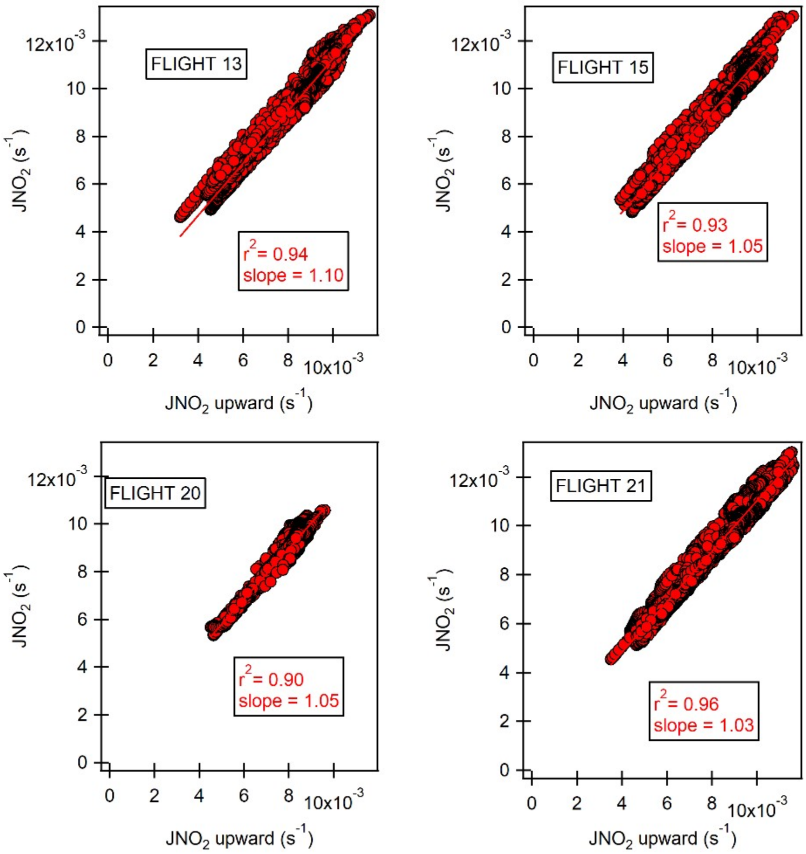

Figure S1: Relationship between $J(NO_2)_{total}$ and $J(NO_2)_{upward}$ from marine flights of ChArMEx aircraft campaign in summer 2014.

Table S2: Flights selected for this study

	Flight number	Date	Local Time	Ozone level	Sector and/or type
MEGAPOLI	25	07/01/2009	11:39:40-15:27:36	Very important Mean : 73.6 ppbv	South-West
	27	07/10/2009	11:08:43-14:58:02	Low Mean : 39.3 ppbv	East
	30	07/16/2009	11:41:26-15:21:45	Important Mean : 52.5 ppbv	North
	32	07/21/2009	11:04:31-14:47:50	Important Mean : 60.1 ppbv	North
	33	07/25/2009	11:02:01-16:47:10	Low Mean :31.1 ppbv	East
	36	07/29/2009	11:40:02-15:23:11	Important Mean : 52.5 ppbv	North
DACCIWA	19	07/01/2016	10:22:24-13:49:12	Low Mean : 34.4 ppbv	Cloud, Accra city, Biogenic
	32	07/12/2016	13:38:24-16:58:24	Low Mean : 37.4 ppbv	Cloud, Accra City, Biogenic, Biomass-Burning
	36	07/16/2016	11:34:48-14:52:00	Low Mean : 34.8 ppbv	Cloud, Accra City
SAFMED	46	07/24/2013	12:49:14-14:58:16	Important Mean : 63.7 ppbv	Genova-Cagliari
	47	07/24/2013	16:46:50-18:14:35	Important Mean :63.7 ppbv	Tyreman sea

Table S3: Values of the rate constants used in the calculation of the Leighton ratio.

	K_{O3+NO} $(cm^3 molecule^{-1} s^{-1})$				K_{HO2+NO} $(cm^3 molecule^{-1} s^{-1})$			
Flights	Min $\times 10^{-14}$	Max $\times 10^{-14}$	Mean $\times 10^{-14}$	STD $\times 10^{-15}$	Min $\times 10^{-12}$	Max $\times 10^{-12}$	Mean $\times 10^{-12}$	STD $\times 10^{-14}$
MEGAPOLI								
25	1.35	2.04	1.81	1.00	8.10	8.72	8.28	9.18
27	1.20	1.67	1.54	9.01	8.40	8.92	8.54	9.95
30	1.30	1.95	1.76	1.21	8.17	8.78	8.33	11.6
32	1.33	2.03	1.84	1.19	8.10	8.75	8.26	10.8
33	1.48	1.72	1.62	2.49	8.35	8.58	8.45	2.35
36	1.31	1.89	1.73	8.93	8.22	8.77	8.35	8.52
SAFMED								
46&47	1.79	1.96	1.90	3.10	8.16	8.30	8.21	2.44
DACCIWA								
19	1.64	2.08	1.92	9.40	8.08	8.43	8.19	7.54
32	1.59	2.07	1.91	1.10	8.08	8.48	8.20	9.04
36	1.63	2.18	1.93	1.28	8.00	8.44	8.19	10.5

Table S4: Statistics of the Leighton ratio values found in this study inside and outside the plume. The **Φ** values are reported during the whole flight and in the plume and the percentages within, lower and higher than PSS±σ [0.68-1.32]. The magnitude of rapid changes in NO,NO_2, ozone and $J(NO_2)$ are also reported when detected. A rapid change corresponds to a relative difference higher than 20% between two consecutive airborne data.

N°	**Φ range during the whole flight**	**MEGAPOLI : inside the plume**			
		[NOx] threshold Φ range Φ mean	**Φ values within PSS [0.68–1.32]**	**Φ values < 0.68** (PSS–σ) Detected rapid changes in the Φ calculation terms	**Φ values > 1.32** (PSS+σ) Detected rapid changes in the Φ calculation terms
25	[0.35-20.07]	[NOx] > 4.5 ppbv Φ ∈ [0.41-1.46] Mean : 0.83 ±0.30	**52.6 %**	**36.8 %** Rapid change [NO] : up to 74%. [NO_2]: up to 52 %	**10.5 %** Rapid change : [NO] : 42 and 74%. [NO_2] 21 and 31%
27	[0.30-9.82]	NOx > 3 ppbv Φ ∈ [0.81-2.89] Mean : 1.85 ±0.51	**7.9 %**	**0%**	**92.1%** Rapid change: $J(NO_2)$: up to 77% [NO] : up to196 % [NO_2]: up to 1060 %
30	[0.12-3.92]	NOx > 3 ppbv Φ ∈ [0.61-1.35] Mean : 0.95 ±0.17	**90%**	**5 %** Rapid change: $J(NO_2)$: up to 26 % [NO] up to 33 % [NO_2] up to 34 %	**5%** Rapid change $J(NO_2)$: up to 72 % [NO_2] up to 63 %
32	[0.16-2.83]	NOx > 2 ppbv Φ ∈ [0.57-1.03] Mean : 0.77±0.11	**77.6 %**	**22.4 % ; 14.3 % can be explained by :** Rapid change $J(NO_2)$: up to 26 % [NO] : up to 78 % [NO_2]: up to 62 %	**0%**
33	[0.52-5.11]	NOx > 2.5 ppbv Φ ∈ [0.75-3.93] Mean : 1.93 ±0.69	**12.7 %**	**0 %**	**87.3 % ; 54 % can be explained by** Rapid change $J(NO_2)$: up to 116% [NO] : up to 101% [NO_2] : up to 105 %
36	[0.51-4.92]	NOx > 3 ppbv Φ ∈ [0.51-1.08] Mean : 0.71 ±0.12	**43.14 %**	**56.86 % Where 33.33% are linked to** Rapid change: $J(NO_2)$: up to 20 % [NO] : up to 103 % [NO_2] :up to 61 % 23.5% of the data are not linked to any of these	**0%**

N°	Φ range during the whole flight	CHARMEX/SAFMED : inside the plume			
		[NOx] threshold Φ range Φ mean	**Φ values within PSS [0.68–1.32]**	**Φ values < 0.68** (PSS–σ) Detected rapid changes in the Φ calculation terms	**Φ values > 1.32** (PSS+σ) Detected rapid changes in the Φ calculation terms
46	[[0.60-1.78]	NA Mean : 1.08 ±0.30	**89.5 %**	**1.9 %** Rapid change: [NO] : up to 154 % $[NO_2]$: up to 75 %	**8.6 %** Rapid change [NO] : up to 58 %
47	[4.74-8.67]	NA 7.13 ± 1.44	**0.0%**	**0.0%**	**100 %**

N°	Φ range during the whole flight	DACCIWA : inside the plume			
		[NOx] threshold Φ range Φ mean	**Φ values within PSS [0.68–1.32]**	**Φ values < 0.68** (PSS–σ) Detected rapid changes in the Φ calculation terms	**Φ values > 1.32** (PSS+σ) Detected rapid changes in the Φ calculation terms
19	[0.06-10.5]	NOx > 4.5 ppbv Φ ∈ [0.18-5.17] Mean : 1.74 ±1.24	**45%**	**10%** Rapid change: [NO] : up to 7000% $[NO_2]$: up to 1250 %	**45 %** Rapid change $[O_3]$: 19% [NO] : up to 46 %
32	[0.12-8.60]	NOx > 4 ppbv Φ ∈ [0.60-2.85] Mean : 1.59±0.55	**33.3%**	**6.7 %** Rapid change: [NO] : 20% $[NO_2]$: 24%	**60 %** Rapid change: [NO] up to 652 %
36	[0.13-7.03]	NOx > 1.5 ppbv Φ ∈ [1.19-4.01] Mean : 1.79±0.71	**16.7 %**	**0%**	**83.3 %** **61.1 % are linked to** Rapid change: $J(NO_2)$: up to 23 % [NO] : up to 56 % $[NO_2]$: up to 52 %

Table S5: Aggregated values of the Leighton ratio from previous studies reported in the literature.

Type	Location	Period	Φ	References
Urban plume	Sarnia, Ontario, Canada	March 2017	0.44-1.61	1
Urban **Clear sky**	New Delhi, India	October, 2014 May 2014	0.3-3.6 (mean = 1.01±0.52) 0.4-2.6 (mean = 0.89±0.4)	2
Urban	New Delhi, India	December 2012	0 0.8	3
Urban plume **Clean remote**	Amazonas State, Brazil	July 2001	< 2 2.5-16	4
Urban	Sakai City , Japan	August, 2002	0.5-1.3	5
Highly polluted airmass	North Norfolk Coast	November 1993 October 1994	1 Up to 2	6
Urban	Claremont, California	September 1980	0.3 – 2.1	7
Urban, High sun	Hawai	Spring 1988	≈ 2	8
Urban, High sun	Hawai	All seasons 1991-1992	1.5-2	9
Aircraft	Western and central North Pacific	October 1991	Median = 2.36	10
Aircraft	Subtropical/tropical North and South Atlantic Ocean	August – September 1989	0.9-3 (mean)	11
Remote Farmland, plants	Backgarden Kaiping	Summer Autumn	2.3 ± 0.4 3.1 ± 1.4	12
Clean background	South Atlantic ocean	March 2007	Up to 15	13
Farm (low NOx area)	New England	Summer 2004	1-5.9	14
Rural	Germany	March 1999-Decamber 2002	2.5 – 5.7	15
Rural	Germany	Summer 1998	1.1-1.5 for NO > 1 ppb 2 for NO < 1 ppb	16
Rural Agricultural site	Germany	August 1994	Mean =1.2, Max =1.85	17
Rural	Alabama, USA	July 1990	<2	18

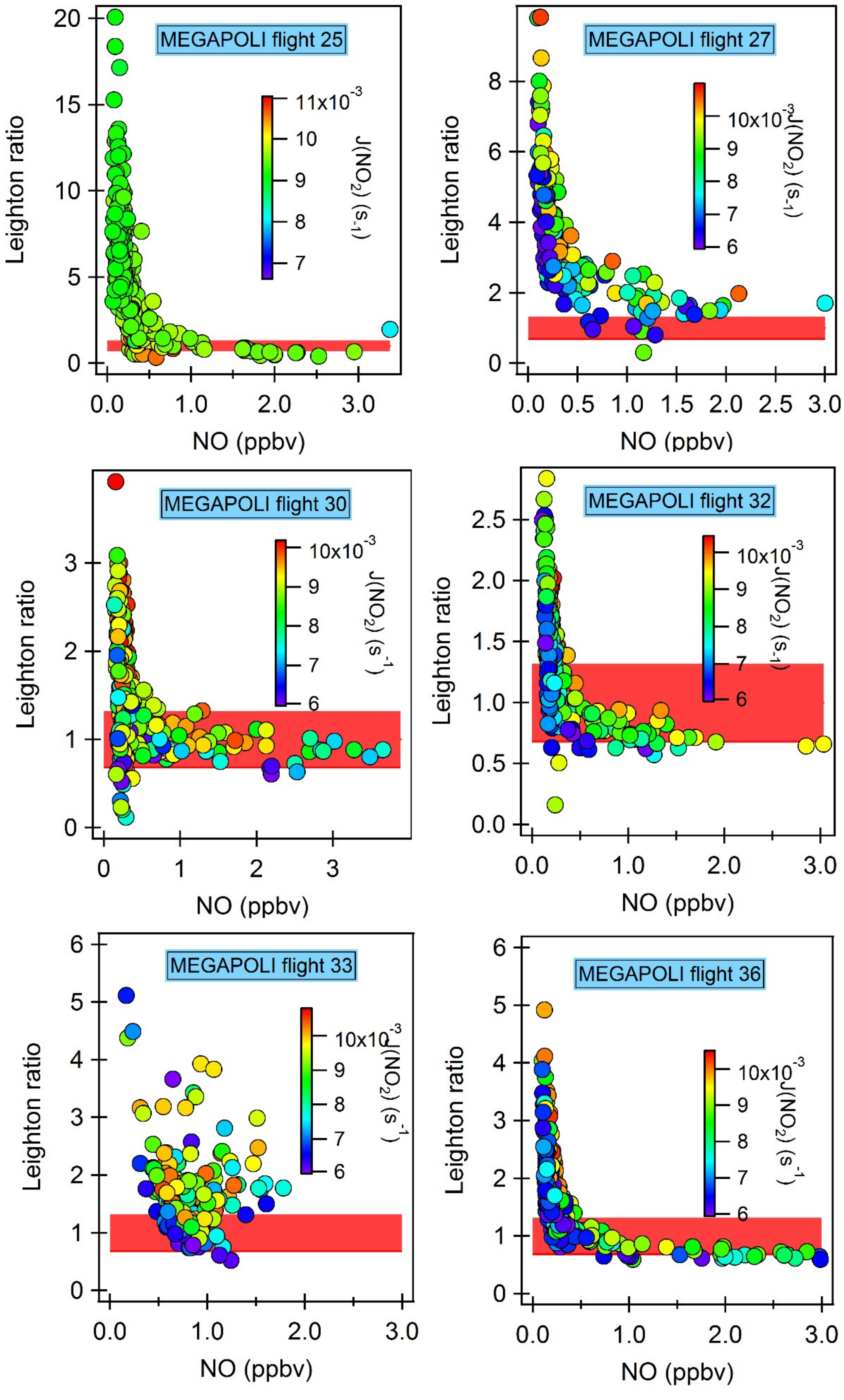

Figure S6 : Dependence of the Leighton ratio on NO during MEGAPOLI. Scatterplots are color-coded with JNO$_2$ The red area corresponds to the PSS at ±0.32.

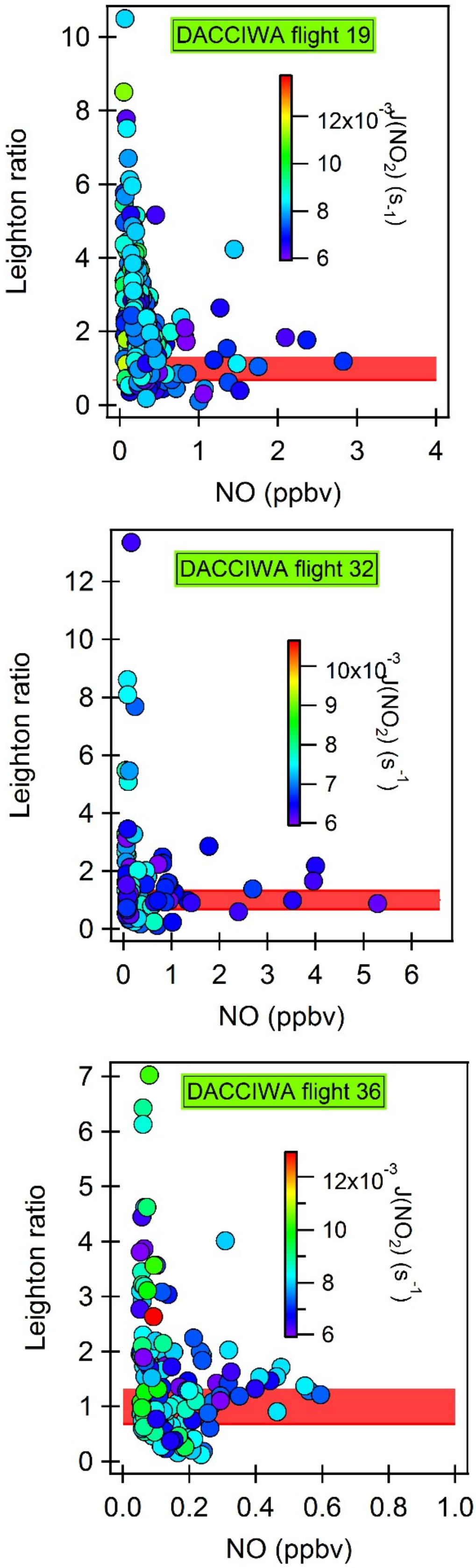

Figure S7: Dependence of the Leighton ratio on NO during DACCIWA. . Scatterplots are color-coded with *J*NO_2 The red area corresponds to the PSS at ±0.32

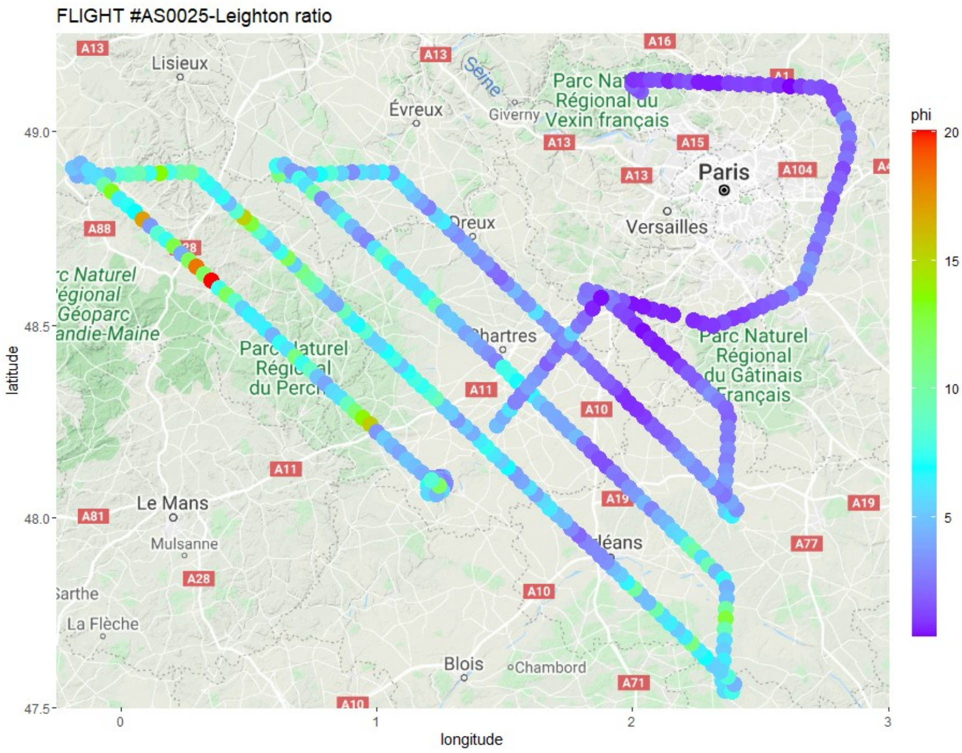

Figure S8: Plot trajectories of the Leighton ratio in Paris and in SWA

<u>Table S6</u>: Aggregated values of maximum peroxy radical mixing ratio and PO_3 found inside and outside the urban plumes**.**

		Inside the plumes		Outside the plumes	
	Flights	**[ROx]max in ppt**	**PO_3max in ppbv/h**	**[ROx]max in ppt**	**PO_3max in ppbv/h**
MEGAPOLI	**25**	No production	No production	331.4	120
	27	95.3	99.4	572	56.5
	30	21.2	13.4	230.2	33.2
	32	No production	No production	199	21.5
	33	129.0	86.4	117.5	47.2
	36	No production	No production	389.6	32.7
DACCIWA	**19**	67.0	111.5	102.3	17.4
	32			115.0	9.7
	36	247.9	27.6	49.1	4.8
SAFMED	**46**	110.9	18.0	Non determined	Non determined

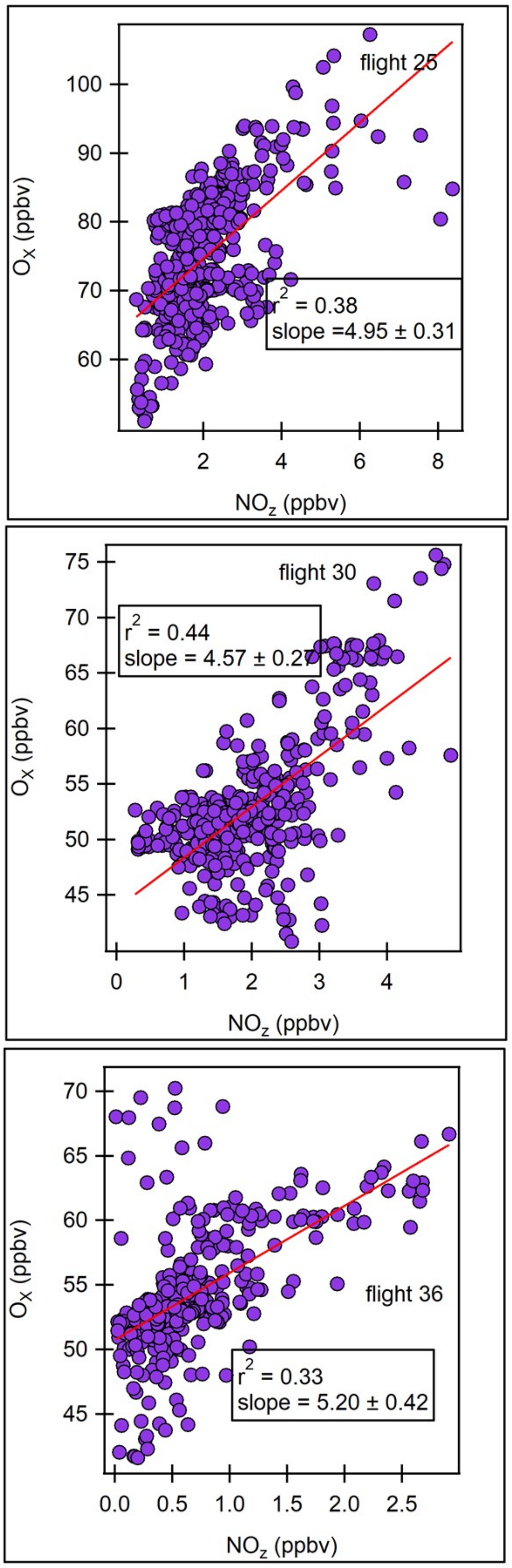

Figure S9: Ox (= $O_3 + NO_2$) versus NO_z for flights 25, 27, 32 and 36 during MEGAPOLI.

Table S7: Aggregated values of OPE found in previous studies

Location	Type	Period	OPE	References
Beijing, China	Urban	August 2008	[3.9-9.7]	[19]
	Mountain, rural	July 2005	[3 – 6]	[20]
	Urban	August 2008	8	[21]
Scottia, Pennsylvania	Low NOx, rural	Summer 1988	8.5	[22]
Phoenix, Arizona	Urban (aircraft)	May and June 1998	2.7	[23]
Beijing, China	Urban	1.1	Winter 2007	[24]
Nashville, Tennessee	Urban plume	[2.5 – 4]	July 1995	[25]
New York states	Rural site in Addison Rural site in Witmington	2000 – 2015 2015 – 2017	[5 - 13] 18	[26]
Beijing, China	Urban	Summer 2012	1-6.8	[27]
Durham, New Hampshire	Rural	August 2002	[7.7 – 9.7]	[28]
Beijing, China	Urban plume Rural plume	Summer 2008	4 5.3	[29]
Nashville, New York	Rural Urban	July 1996	10 [2 – 4]	[30]
Tennessee	Power plant plume	July, 7 1998	[1.2-2.5]	[31]
Los Angeles, California	Urban	May – june 2010	3.9 – 4.7	[32]
South USA	Urban Suburban rural	1996 - 2015	[2 - 3] 2 [1-2]	[33]

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