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Supplement of

Tropospheric chemistry in the Integrated Forecasting System of ECMWF

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Supplement Tables

Table A1 Species of CB05 in C-IFS, if subject to wet and dry deposition and the Henry's law coefficicnet (H_A) and Heat of Dissolution (Δ H_A) at 298 K

Short name	**Long name**	**Dry Depo-sition**	**Wet Depo-sition**	**Molar Mass (g/mol)**	**H_A (M / atm)**	**Δ H_A *(kcal / mol)***
O3	ozone	yes	no	48	0	0
H2O2	hydrogen peroxide	yes	yes	34	8.30E+04	7400
CH4	methane	no	no	16	0	0
CO	carbon monoxide	yes	yes	28	9.90E-04	1300
HNO3	nitric acid	yes	yes	63	3.20E+11	8700
CH3OOH	methylperoxide	yes	yes	48	3.10E+02	5200
HCHO	formaldehyde	yes	yes	30	3.20E+03	6800
PAR	paraffins	no	no	12	0	0
C2H4	ethene	no	no	28	0	0
OLE	olefins	no	no	24	0	0
ALD2	aldehydes	true	yes	24	17	5000
PAN	peroxyacetyl nitrate	yes	yes	121	8.00E+00	6500
ROOH	peroxides	yes	yes	47	340	6000
ONIT	organic nitrates	yes	yes	77	7.50E+03	6485
C5H8	isoprene	no	no	68.1	0	0
SO2	sulfur dioxide	yes	yes	64.1	1.00E+05	3000

DMS	dimethyl sulfide	no	no	62.1	0	0
NH3	ammonia	yes	yes	17	75	3400
SO4	sulfate	yes	yes	96.1	3.20E+11	8700
NH4	ammonium	no	yes	18	3.20E+11	8700
MSA	methanesulfonic acid	no	yes	96.1	3.20E+11	8700
CH3COCHO	methylglyoxal	true	true	72.1	3.20E+04	8700
O3S	stratospheric ozone	true	no	48	0	0
Rn	radon	no	no	222	0	0
Pb	lead	no	yes	210	3.20E+11	8700
NO	nitrogen monoxide	yes	yes	30	1.90E-03	1400
HO2	hydroperoxy radical	no	yes	33	4.00E+03	5900
CH3O2	methylperoxy radical	no	no	47	0	0
OH	hydroxyl radical	no	no	17	0	0
NO2	nitrogen dioxide	true	yes	46	1.20E-02	2500
NO3	nitrate radical	yes	yes	62	2.00E+00	2000
N2O5	dinitrogen pentoxide	yes	yes	76	2.10E+01	3400
HO2NO2	pernitric acid	yes	yes	79	1.20E+04	6900
C2O3	peroxyacetyl radical	no	no	75	0	0
ROR	organic ethers	no	no	28	0	0

RXPAR	PAR budget corrector	no	no	12	0	0
XO2	NO to NO2 operator	no	no	44	0	0
XO2N	NO to alkyl nitrate operator	no	no	44	0	0
NH2	amine	no	no	16	0	0
PSC	polar stratosph cloud	no	no	1	0	0
CH3OH	methanol	yes	yes	31.01	220	5200
HCOOH	formic acid	true	true	46.01	8.90E+03	6100
MCOOH	methacrylic acid	true	true	62.02	4.10E+03	6300
C2H6	ethane	no	no	30.02	0	0
C2H5OH	ethanol	yes	yes	46.02	190	6600
C3H8	propane	no	no	44.03	0	0
C3H6	propene	no	no	42.03	0	0
C10H16	terpenes	no	no	136	0	0
ISPD	methacrolein MVK	yes	no	70	0	0
NO3 A	nitrate	true	yes	62	3.20E+11	8700
CH3COCH3	acetone	no	true	58	35	3800
ACO2	acetone product	no	no	58	0	0
IC3H7O2	(CH3)2CHO2	no	no	75	0	0
HYPROPO2	product from C3H6+OH	no	no	91	0	0

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Table A2 The chemical mechanism as applied in C-IFS (CB05). The reaction products O_2, CO_2 and H_2O are not shown. All reactions of the NH2 radical act as sink processes for the respective radicals and oxidants. The source of the rate data is as follows: [1] Yarwood et al. (2005), [2] Sander et al. (2011), [3] IUPAC datasheet (http://iupac.pole-ether.fr), [4] Archibald et al. (2010) [5] Zaveri and Peters (1999), [6] Atkinson et al. (2006), [7] Williams et al. (2013), [8] Houweling et al. (1998), [9] Horowitz et al.(2003), [10] Atkinson et al. (2004), [11] Emmons et al. (2010), [12] Huijnen, Williams and Flemming (2014).

Reactants	Products	Rate Expression	Reference
$NO + O_3$	NO_2	3.0E-12*exp(-1500/T)	[1]
$NO + HO_2$	$NO_2 + OH$	3.5E-12*exp(250/T)	[1]
$NO + CH_3O_2$	$HCHO + HO_2 + NO_2$	2.8E-12*exp(300/T)	[1]
$NO_2 + OH$ (+ M)	HNO_3	K_0 = 1.8E-30*$(300/T)^{3.0}$ K_∞ = 2.8E-11	[1],[2]
$OH + HNO_3$	NO_3	K_0 = 2.41E-14*(460/T) K_2 = 2.29E-17*(2199/T) K_3 = 6.51E-14*(1336/T)	[1],[2]
$NO_2 + O_3$	NO_3	1.2E-13*exp(-2540/T)	[1]
$NO + NO_3$	$NO_2 + NO_2$	1.5E-11*exp(170/T)	[1]
$NO_2 + NO_3$	N_2O_5	K_0 = 2.0E-30*$(300/T)^{4.4}$ K_∞ = 1.4E-12*$(300/T)^{0.7}$	[1],[2]
N_2O_5	$NO_2 + NO_3$	2.7E-27*exp(11000/T)	[1],[2]
$OH + HNO_4$	NO_2	1.3E-12*exp(380/T)	[1] ,[2]
$NO_2 + HO_2$	HNO_4	K_0 = 2.0E-31*$(300/T)^{3.4}$ K_∞ = 2.9E-12*$(300/T)^{1.1}$	[1] ,[2]
HNO_4 (+ M)	$NO_2 + HO_2$	2.1E-27*exp(10900/T)	[1] ,[2]
$O(^1D)$ (+ M)		3.3E-11*exp(55/T)*[O_2] + 2.15E11*exp(110/T)*[N_2]	[1] ,[2]
$O(^1D) + H_2O$	$OH + OH$	1.63E-10*exp(60/T)	[1] ,[2]
$O_3 + HO_2$	OH	1.0E-14*exp(-490/T)	[1]
$CO + OH$	HO_2	K_0 = 5.9E-33*$(300/T)^{1.4}$ K_∞ = 1.1E-12*$(300/T)^{-1.3}$ K_0 = 1.5E-13*$(300/T)^{-0.6}$ K_∞ = 2.1E9*$(300/T)^{-6.1}$	[1],[2]
$O_3 + OH$	HO_2	1.7E-12*exp(-940/T)	[1]
$OH + H_2O_2$	HO_2	1.8E-12	[1]

OH + HCHO	CO + HO_2	5.5E-12*exp(125/T)	[1]
OH + CH_4	CH_3O_2	2.45E-12*exp(-1775/T)	[1]
OH + CH_3OOH	0.7 CH_3O_2 + 0.3 HCHO + 0.3 OH	3.8E-12*exp(200/T)	[1]
OH + ROOH	0.77 XO_2 + 0.19 CH3COCHO + 0.04 ALD2 + 0.23 OH + RXPAR	2E-11	[4],[5]
CH_3O_2 + HO_2	CH_3OOH	4.1E-13*exp(750/T)	[1]
CH_3O_2 + CH_3O_2	1.37 HCHO + 0.74 HO_2 + 0.63 CH_3OH	9.5E-14*exp(390/T)	[2],[5]
OH + HO_2		4.8E-11*exp(250/T)	[1]
HO_2+ HO_2	H_2O_2	3.5E-13*exp(430/T) 1.77E-33*exp(1000/T) 1.4E-21*exp(2200/T)	[1],[2]
OH + H_2	HO_2	2.8E-12*exp(-1800/T)	[1]
NO_3 + HCHO	HNO_3 + CO + HO_2	5.8E-16	[1]
ALD2 + OH	C_2O_3	Average of : 4.4E-12*exp(365/T) 5.1E-12*exp(405/T)	[1],[6]
ALD2 + NO_3	C_2O_3 + HNO_3	Average of : 1.4E-12*exp(-1860/T) 6.4E-15	[1],[6]
NO + C_2O_3	CH_3O_2 + NO_2	8.1E-12*exp(270/T)	[1]
NO_2 + C_2O_3	PAN	K_0 = 2.7E-28*(300/T) $^{7.1}$ K_∞ = 1.2E-11*(300/T) 0.9	[3]
PAN	NO_2 + C_2O_3	K_0 = 4.9E-3*exp(-12100/T) K_∞ = 5.4E16*exp(-13830/T)	[1],[6]
NO_3 + HO_2	HNO_3	4.0E-12	[1],[3]
NO_3 + CH_3O_2	NO_2 + HO_2 + HCHO	1.2E-12	[3],[5]
NO_3 + C_2O_3	NO_2 + CH_3O_2	4.0E-12	[5]
NO_3 + XO_2	NO_2	2.5E-12	[5]
OH + CH_3OH	HCHO + HO_2	2.85E-12*exp(-345/T)	[1],[3]
OH + HCOOH	HO_2	4.0E-13	[1]
OH + C_2H_6	0.991ALD2+0.991XO2+0.009XP2N+ HO2	6.9E-12*exp(-1000/T)	[1],[6]
OH + C_2H_5OH	ALD2 + HO_2 + 0.1 XO_2 + 0.1HCHO	3.0E-12*exp(20/T)	[1],[3]
OH +CH_3COOH	CH_3O_2	4.2E-14*exp(-855/T)	[1],[6]
OH + C_3H_8	IC3H7O2	7.6E-12*exp(-585/T)	[3,11]
$IC_3H_7O_2$ + NO	0.82 CH_3COCH_3 + HO_2 +0.27 ALD2 + NO_2	4.2E-12*exp(180/T)	[11]
$IC_3H_7O_2$ + HO_2	ROOH	7.5E-13*exp(700/T)	[11]
OH + C_3H_6	HYPROPO2	ko =8.0E-27 *(-300/T)$^{3.5}$ k_∞ = 3.0E-11	[3,11]
HYPROPO2 +NO	ALD2 + HCHO + HO_2 + NO_2	4.2E-12*exp(180/T)	[11]
HYPROPO2 +HO_2	ROOH	7.5E-13*exp(700/T)	[11]
O_3 + C_3H_6	0.54HCHO + 0.19HO_2 + 0.33OH + 0.56CO + 0.5ALD2 + 0.31CH_3O_2 + 0.25HCOOH	5.5E-15*exp(-1880/T)	[6,9]
NO_3 + C_3H_6	ORGNTR	4.6E-13*exp(-1155/T)	[6,9]
C_2O_3 + C_2O_3	2 CH_3O_2	2.9E-12*exp(500/T)	[1]

$C_2O_3 + HO_2$	$0.4\ CH_3COOH + 0.4\ O_3$	4.3E-13*exp(1040/T)	[5]
OH + PAR	$0.87\ XO_2 + 0.76\ ROR + 0.11\ HO_2 + 0.11\ ALD2 + 0.11\ RXPAR + 0.13\ XO_2N$	8.1E-13	[1],[8]
ROR	$1.1\ ALD2 + 0.96\ XO_2 + 0.04\ XO_2N + 0.02\ ROR + 2.1\ RXPAR + 0.94\ HO_2$	1E15*exp(-8000/T)	[4]
ROR	HO_2	1600.0	[1]
OH + OLE	$0.8\ HCHO + 0.95\ ALD2 + 0.8\ XO_2 + 1.57HO_2 +0.7\ RXPAR + 0.62\ CO$	5.2E-14*exp(-610/T)	[1],[7]
O_3 + OLE	$0.5\ ALD2 + 0.74\ HCHO + 0.76\ HO_2 + 0.22\ XO_2 + 0.95\ CO + RXPAR + 0.1\ OH$	8.5E-16*exp(1520/T)	[1],[7]
NO_3 + OLE	$0.91\ XO_2 + HCHO + 0.09\ XO_2N + NO_2 + 0.91\ ALD2 + RXPAR + 0.56\ HO_2 + 0.56\ CO$	4.6E-14*exp(400/T)	[1],[2]
$OH + C_2H_4$ (+M)	$HO_2 + 1.56\ HCHO + 0.22\ ALD2 + XO_2$	K_0 = 1.0E-28*(300/T) $^{4.5}$ K_∞ = 8.8E-12*(300/T) 0.85	[1],[2]
$O_3 + C_2H_4$	$HCHO + 0.22\ HO_2 + 0.12\ OH + 0.24\ CO + 0.52\ HCOOH$	1.2E-14*exp(-2630/T)	[5]
$OH + CH_3COCHO$	$XO_2 + C_2O_3$	1.5E-11	[6]
OH + C10H16	$1.22HO_2 + 1.25XO_2 + 0.25XO_2N + 1.22HCHO + 5.0PAR + 0.47ALD2 + 0.47CO$	1.2E-11*exp(440/T)	[3],[7]
O_3 + C10H16	$0.57OH + 0.28HO_2 + 0.76XO_2 + 0.18XO_2N + 1.8HCHO + 0.211CO +$ 6.0PAR + 0.21ALD2 + 0.39C2O3 + 0.39CH3O2	6.3E-16*exp(-580/T)	[3],[7]
NO_3 + C10H16	$0.47NO_2 + 0.75HO_2 + 1.03XO_2 + 0.25XO_2N + 0.47ALD2 +$ 0.53ORGNTR + 0.47CO + 6.0PAR	1.2E-12*exp(490/T)	[3,7]
OH + ISOP	$0.4\ ISPD + 0.\ 7\ XO_2 + 0.629\ HCHO + 0.5\ HO_2 + 0.088\ XO_2N$	2.7E-11*exp(390/T)	[4,12]
O_3 + ISOP	$0.65\ ISPD + 0.6\ HCHO + 0.066\ CO + 0.2\ C_2O_3 + 0.15\ ALD2 + 0.35\ PAR + 0.066\ HO_2 + 0.2\ XO_2 + 0.266\ OH$	1.04E-14*exp(-1995/T)	[3],[7]
NO_3 + ISOP	$0.2\ ISPD + 0.8\ HO_2 + 0.8\ ORGNTR + 0.8\ ALD2 + 2.4\ PAR + 0.2\ NO_2 + XO_2$	3.15E-12*exp(-450/T)	[3],[7]
OH + ISPD	$1.565PAR + 0.167HCHO + 0.503HO_2 + 0.334CO + 0.168CH_3COCHO + 0.273ALD2 + 0.498C_2O_3 + 0.713XO_2$	Average of: 1.86E-11*exp(175/T) 2.6E-12*exp(610/T)	[1],[7]
O_3 + ISPD	$0.114C_2O_3 + 0.15HCHO + 0.85\ CH_3COCHO + 0.154HO_2 + 0.268OH + 0.064XO_2 + 0.02ALD2 + 0.36PAR + 0.225CO$	Average of: 8.5E-16*exp(-1520/T) 1.4E-15*exp(-2100/T)	[3],[7]

NO_3 + ISPD	0.357ALD2 + 0.282HCHO + 1.282PAR + 0.925HO_2 + 0.643CO + 0.85ORGNTR + 0.075C_2O_3 + 0.075XO_2 + 0.15HNO_3	Average of: 6.0E-16 3.4E-15	[3],[7]
OH + CH3COCH3	ACO2	8.8E-12*exp(-1320/T)+ 1.7E-14*exp(423/T)	[3],[7]
ACO2+HO2	ROOH		[3],[7]
ACO2+CH3O2	0.5 CH3OH + 0.5HO2 +0.7ALD2 + 0.2C2O3 + 0.5CH3COCHO		[6],[7]
ACO2+NO	NO2 + C2O3 + HCHO + HO2		[6],[7]
OH + ORGNTR	NO_2 + XO_2	5.9E-13*exp(-360/T)	[7]
NO + XO_2	NO_2	2.6E-12*exp(365/T)	[1]
XO_2 + XO_2		1.6E-12*exp(-2200/T)	[1]
XO2+XO2N		6.8E-14	[1]
XO2N+XO2N		6.8E-14	[1],[6]
NO + XO_2N	ORGNTR	2.6E-12*exp(365/T)	[1]
HO_2 + XO_2	ROOH	7.5E-13*exp(700/T)	[1]
PAR + RXPAR		8E-11	[8]
HO_2 + XO_2N	ROOH	8E-12*exp(-2060/T)	[1]
DMS + OH	SO_2	1.1E-11*exp(-240/T)	[1]
DMS + OH	0.75 SO_2 + 0.25 MSA	1.0E-39*exp(5820/T) 5.0E-30*exp(6280/T)	[2]
DMS + NO_3	SO_2	1.9E-13*exp(520/T)	[10]
OH + SO_2	SO_4^{2-}	K_0 = 3.3E-31*(300/T)$^{4.3}$ K_∞ = 1.6E-12*(300/T)	[2]
OH + NH_3	NH_2	1.7E-12*exp(-710/T)	[2]
NO + NH_2		4.0E-12*exp(450/T)	[2]
NO_2 + NH_2		2.1E-12*exp(650/T)	[2]
HO_2 + NH_2		3.4E-11	[2]
O_2 + NH_2		6.0E-21	[2]
O_3 + NH_2		4.3E-12*exp(-930/T)	[2]

Table A3 Photolysis reactions in as applied in C-IFS (CB05). The reaction products O_2 and H_2O are not shown. The stoichiometry of each photolytic reaction is taken from Yarwood et al. (2005) except for the photolysis of O_2. The absorbtion coefficients and quantum yields are taken from [1] Sander et al. (2011), [2] Matsumi et al. (2002) and [3] Atkinson et al. (2006). Further details are given in Williams et al., (2013).

Stoichiometry		Reference
$O_3 + hv \rightarrow$	$O(^1D)$	[1,2]
$NO_2 + hv \rightarrow$	$NO + O_3$	[1]
$H_2O_2 + hv \rightarrow$	2OH	[1]
$HNO_3 + hv \rightarrow$	$OH + NO_2$	[1]
$HNO_4 + hv \rightarrow$	$HO_2 + NO_2$	[1]
$N_2O_5 + hv \rightarrow$	$NO_2 + NO_3$	[1]
$HCHO + hv \rightarrow$	CO	[3]
$HCHO + hv \rightarrow$	$CO + 2HO_2$	[3]
$CH_3OOH + hv \rightarrow$	$HCHO + HO_2 + OH$	[1]
$NO_3 + hv \rightarrow$	$NO_2 + O_3$	[1]
$NO_3 + hv \rightarrow$	NO	[1]
$PAN + hv \rightarrow$	$C_2O_3 + NO_2$	[1]
$ORGNTR + hv \rightarrow$	$NO_2 + 0.51\ XO_2 + 0.3ALD2 + 0.9\ HO_2 + 0.74\ C_2O_3 + 0.74\ CH_3O_2 + 1.98RXPAR$	[3]
$ALD2 + hv \rightarrow$	$HCHO + XO_2 + CO + 2HO_2$	[3]
$CH_3COCHO + hv \rightarrow$	$C_2O_3 + HO_2 + CO$	[1]
$ROOH + hv \rightarrow$	$OH + 0.5\ XO_2 + 0.74C_2O_3 + 0.74\ CH_3O_2 + 0.3\ ALD2 + 0.9HO_2 + 1.98\ RXPAR$	[1]
$ISPD + hv \rightarrow$	$0.333CO + 0.067\ ALD2 + 0.9\ HCHO + 0.832\ PAR + 1.033\ HO_2 + 0.7\ XO_2 + 0.967\ C_2O_3$	[3]
$O_2 + hv \rightarrow$	$2O(^3P)$	[1]
$CH_3COCH_3 + hv \rightarrow$	$CO + 2CH_3O_2$	[3]
$CH_3COCH_3 + hv \rightarrow$	$C_2O_3 + CH_3O_2$	[3]

Table A4 Loss because of dry deposition for 2008 in Tg and as time scale in days with respect to tropospheric burden.

Species	Annual Dry Deposition Loss Tg	Dry deposition time scale in days
NH3	37	1
SO2	78	3
NO3_A	6	4
ISPD	28	6
CH3COCHO	4	7
HNO3	50	7
NO2	17	8
HCHO	35	8
HCOOH	4	10
SO4	15	10
H2O2	106	10
C2H5OH	1	11
ROOH	25	16
CH3OH	74	23
ONIT	13	29
ALD2	1	30
CH3OOH	23	53
MCOOH	31	64
PAN	7	105
HO2NO2	0	110
O3	1124	121
N2O5	0	184

Table A5 Loss because of wet deposition for 2008 in Tg and as time scale in days with respect to tropospheric burden.

Species	Annual Wet Deposition Loss Tg	Wet deposition time scale in days
NO3_A	14	2
SO4	76	2
NH4	22	2
CH3COCHO	9	3
HNO3	90	4
H2O2	260	4
Pb	0	11
HCHO	22	13
ONIT	30	13
HCOOH	3	13
HO2	1	16
SO2	11	19
MCOOH	64	31
MSA	0	35
ROOH	6	68
HO2NO2	1	91
CH3OOH	10	119
C2H5OH	0	163
CH3OH	7	232
NH3	0	832

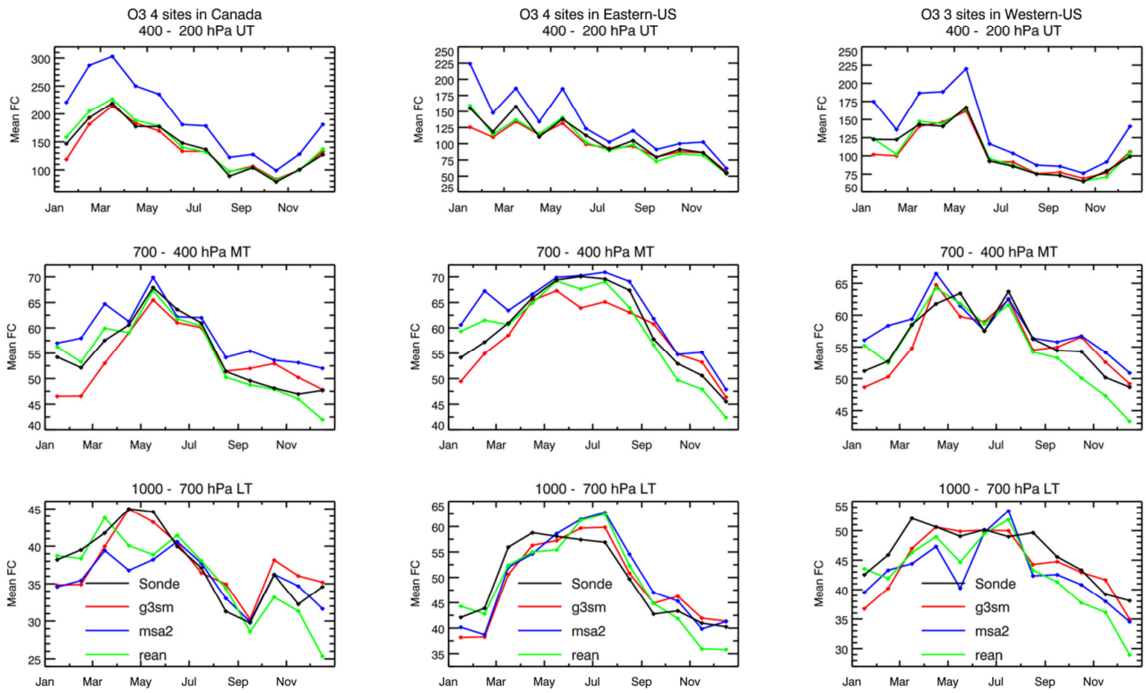

Figure 1 Tropospheric ozone volume mixing ratios (ppb) over the Western-US (right) and Eastern-US (middle) and Canada (left) averaged in the pressure range 1000-700 hPa (bottom), 700-400 hPa (middle) and 400-200 hPa (top) observed by ozonesondes (black) and simulated by C-IFS (red), MOZ (blue) and REAN (green) in 2008

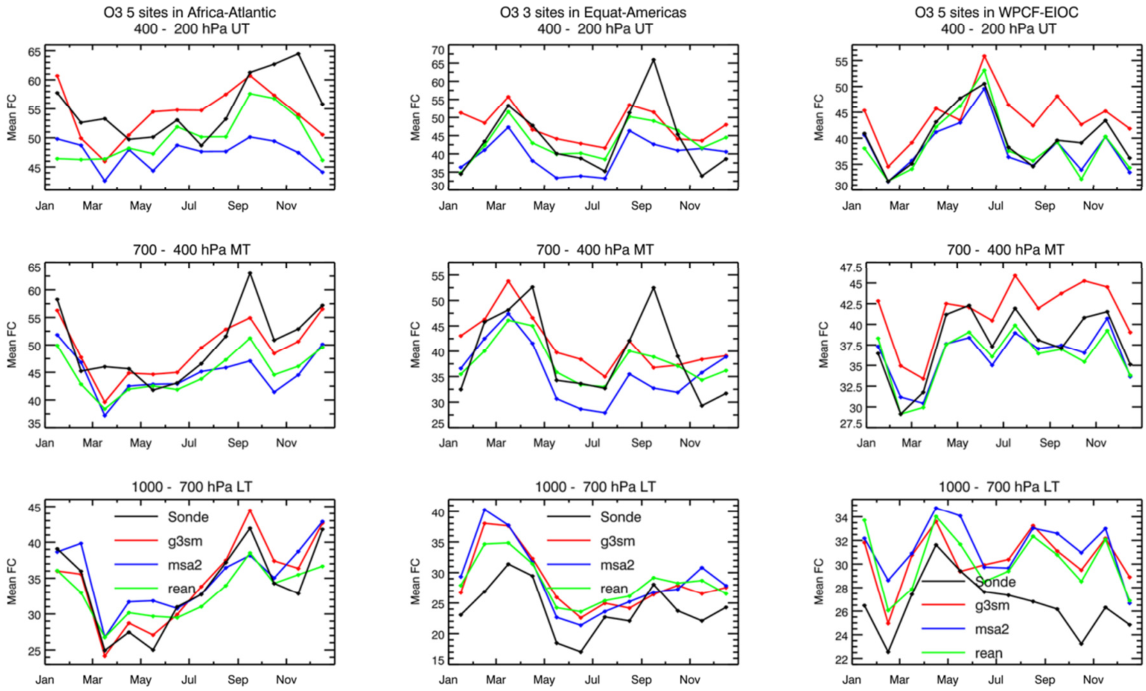

Figure 2 Tropospheric ozone volume mixing ratios (ppb) in the Tropics over Atlantic-Africa region (left) and Eastern Pacific and Indian Ocean (right) and equatorial Americas (middle) averaged in the pressure range 1000-700 hPa (bottom), 700-400 hPa (middle) and 400-200 hPa (top) observed by ozonesondes (black) and simulated by C-IFS (red), MOZ (blue) and REAN (green) in 2008.

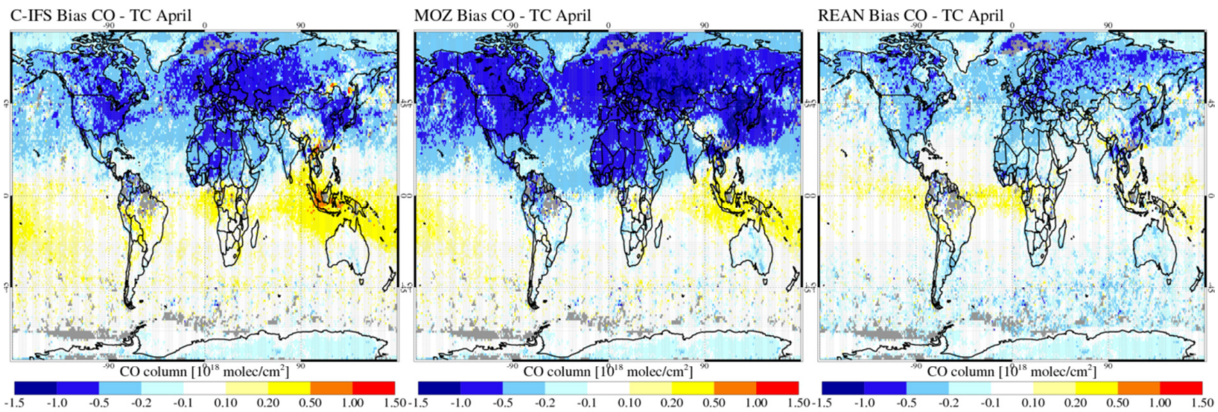

Figure 3 Bias of CO total column with respect to retrieval MOPITT V6 for April 2008 of C-IFS (left), MOZ (middle) and REAN (right).

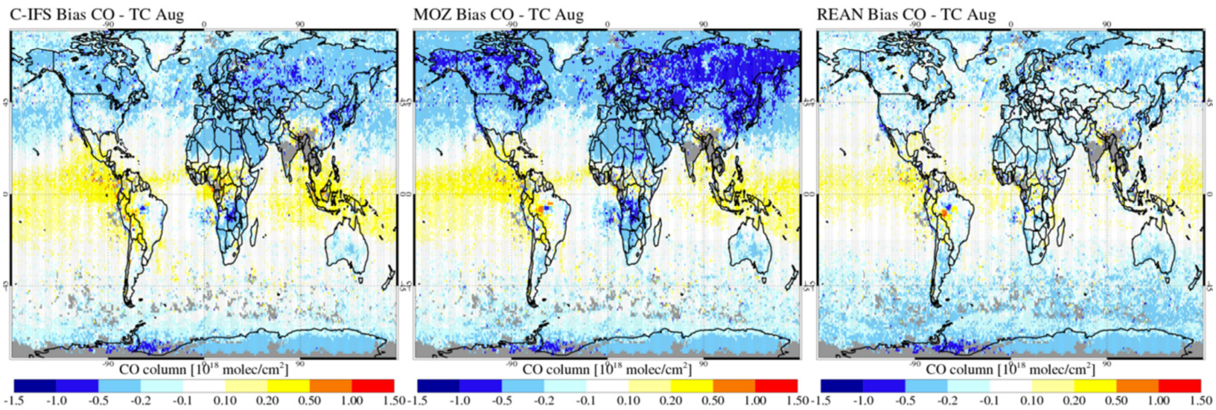

Figure 4 Bias of CO total column with respect to retrieval MOPITT V6 for August 2008 of C-IFS (left), MOZ (middle) and REAN (right)