Supplement of Geosci. Model Dev., 13, 1223–1266, 2020
https://doi.org/10.5194/gmd-13-1223-2020-supplement

Geoscientific Model Development
Open Access
EGU

Supplement of

Description and evaluation of the UKCA stratosphere–troposphere chemistry scheme (StratTrop vn 1.0) implemented in UKESM1

Alexander T. Archibald et al.

Correspondence to: Alexander Archibald (ata27@cam.ac.uk)

Supplementary Information for:

Description and evaluation of the UKCA stratosphere-troposphere chemistry scheme (StratTrop vn 1.0) implemented in UKESM1.

Archibald, Alexander T. [1,2,*], O'Connor, Fiona M. [3], Abraham, N. Luke[1,2], Archer-Nicholls, Scott[1], Chipperfield, Martyn P.[4,5], Dalvi, Mohit [3], Folberth, Gerd A. [3], Dennison, Fraser [4], Dhomse, Sandip S.[4,5], Griffiths, Paul T. [1,2], Hardacre, Catherine[3], Hewitt, Alan J. [3], Hill, Richard[3], Johnson, Colin E.[3], Keeble, James[1,2], Köhler, Marcus O.[1,7,†], Morgenstern, Olaf[6], Mulcahy, Jane P.[3], Ordóñez, Carlos[3,‡], Pope, Richard J.[4,5], Rumbold, Steven T.[8], Russo, Maria R. [1,2], Savage, Nicholas[3], Sellar, Alistair[3], Stringer, Marc[8], Turnock, Steven[3], Wild, Oliver[9] and Zeng, Guang[6].

1) Department of Chemistry, University of Cambridge, Cambridge, UK, CB2 1EW
2) NCAS-Climate, University of Cambridge, UK, CB2 1EW
3) Met Office Hadley Centre, FitzRoy Road, Exeter, UK, EX1 3PB
4) School of Earth and Environment, University of Leeds, Leeds, UK, LS2 9JT.
5) National Centre for Earth Observation (NCEO), University of Leeds, Leeds, U.K.
6) National Institute of Water & Atmospheric Research Ltd (NIWA), 301 Evans Bay Parade, Greta Point, Wellington, New Zealand.
7) Centre for Ocean and Atmospheric Sciences, School of Environmental Sciences, University of East Anglia, Norwich, U.K.
8) NCAS-Climate, Department of Meteorology, University of Reading, Reading, UK, RG6 6BB.
9) Lancaster Environment Centre, Lancaster University, Lancaster, UK, LA1 4YQ

(†) Now at ECMWF, Reading, UK.
(‡) Now at Departamento de Física de la Tierra y Astrofísica, Facultad de Ciencias Físicas, Universidad Complutense de Madrid, Madrid 28040, Spain

*Email: ata27@cam.ac.uk

§1.1 Tables of reactions used in UKCA StratTrop vn 1.0

Table S1. List of bi-molecular reactions in UKCA-StratTrop. Reactions with a † next to them have additional code to account for branching of reaction as, for example, a function of pressure (CO+OH) or H_2O (HO_2 + HO_2). The temperature- dependent rate coefficient can be calculated for each grid box at each chemistry timestep through: $k_{(T)} = A\left(\frac{T}{300}\right)^{\alpha} exp\left(\frac{-Ea}{RT}\right)$ where T refers to the grid box temperature (K).

Reactants	Products	A	α	-Ea/R
Br + Cl_2O_2	BrCl + Cl + O_2	5.90E-12	0	170
Br + HCHO	HBr + CO + HO_2	1.70E-11	0	800
Br + HO_2	HBr + O_2	4.80E-12	0	310
Br + O_3	BrO + O_2	1.60E-11	0	780

Br + OClO	BrO + ClO	2.60E-11	0	1300
BrO + BrO	Br + Br + O_2	2.40E-12	0	-40
BrO + ClO	Br + Cl + O_2	2.30E-12	0	-260
BrO + ClO	Br + OClO	9.50E-13	0	-550
BrO + ClO	BrCl + O_2	4.10E-13	0	-290
BrO + HO_2	HOBr + O_2	4.50E-12	0	-460
BrO + NO	Br + NO_2	8.80E-12	0	-260
BrO + OH	Br + HO_2	1.70E-11	0	-250
CF_2Cl_2 + $O(^1D)$	Cl + ClO	1.40E-10	0	0
$CFCl_3$ + $O(^1D)$	Cl + Cl + ClO	2.30E-10	0	0
Cl + CH_4	HCl + MeOO	7.30E-12	0	1280
Cl + Cl_2O_2	Cl + Cl + Cl	7.60E-11	0	-65
Cl + $ClONO_2$	Cl + Cl + NO_3	6.50E-12	0	-135
Cl + H_2	HCl + H	3.05E-11	0	2270
Cl + H_2O_2	HCl + HO_2	1.10E-11	0	980
Cl + HCHO	HCl + CO + HO_2	8.10E-11	0	30
Cl + HO_2	ClO + OH	3.65E-11	0	375
Cl + HO_2	HCl + O_2	1.40E-11	0	-270
Cl + HOCl	Cl + Cl + OH	3.40E-12	0	130
Cl + NO_3	ClO + NO_2	2.40E-11	0	0
Cl + O_3	ClO + O_2	2.30E-11	0	200
Cl + OClO	ClO + ClO	3.40E-11	0	-160
Cl + MeOOH	HCl + MeOO	5.70E-11	0	0
ClO + ClO	Cl + Cl + O_2	1.00E-12	0	1590
ClO + ClO	Cl + Cl + O_2	3.00E-11	0	2450
ClO + ClO	Cl + OClO	3.50E-13	0	1370
ClO + HO_2	HOCl + O_2	2.60E-12	0	-290

ClO + MeOO	Cl + HCHO + HO_2	3.30E-12	0	115
ClO + NO	Cl + NO_2	6.40E-12	0	-290
ClO + NO_3	Cl + O_2 + NO_2	4.60E-13	0	0
EtCO3 + NO	EtOO + CO_2 + NO_2	6.70E-12	0	-340
EtCO3 + NO_3	EtOO + CO_2 + NO_2	4.00E-12	0	0
EtOO + MeCO3	MeCHO + HO_2 + MeOO	4.40E-13	0	-1070
EtOO + NO	MeCHO + HO_2 + NO_2	2.55E-12	0	-380
EtOO + NO_3	MeCHO + HO_2 + NO_2	2.30E-12	0	0
H + HO_2	H_2 + O_2	6.90E-12	0	0
H + HO_2	$O(^3P)$ + H_2O	1.62E-12	0	0
H + HO_2	OH + OH	7.20E-11	0	0
H + NO_2	OH + NO	4.00E-10	0	340
H + O_3	OH + O_2	1.40E-10	0	470
HO_2 + HO_2†	H_2O_2	3.00E-13	0	-460
HO_2 + MeOO†	MeOOH	3.80E-13	0	-780
HO_2 + NO	OH + NO_2	3.30E-12	0	-270
HO_2 + NO_3	OH + NO_2 + O_2	3.50E-12	0	0
HO_2 + O_3	OH + O_2 + O_2	2.03E-16	4.57	-693
HO_2 + EtCO3	O_2 + EtCO3H	4.40E-13	0	-980
HO_2 + EtCO3	O_3 + EtCO2H	7.80E-14	0	-980
HO_2 + EtOO	EtOOH	6.40E-13	0	-710
HO_2 + ISO2	ISOOH	2.05E-13	0	-1300
HO_2 + MACRO2	MACROOH	1.82E-13	0	-1300
HO_2 + MeCO3	MeCO2H + O_3	7.80E-14	0	-980
HO_2 + MeCO3	MeCO3H	2.13E-13	0	-980
HO_2 + MeCO3	OH + MeOO	2.29E-13	0	-980
HO_2 + $MeCOCH_2OO$	$MeCOCH_2OOH$	9.00E-12	0	0

HO_2 + MeOO†	HCHO	3.80E-13	0	-780
HO_2 + i-PrOO	i-PrOOH	1.51E-13	0	-1300
HO_2 + n-PrOO	n-PrOOH	1.51E-13	0	-1300
i-PrOO + NO	Me2CO + HO_2 + NO_2	2.70E-12	0	-360
i-PrOO + NO_3	Me2CO + HO_2 + NO_2	2.70E-12	0	-360
ISO2 + ISO2	MACR + MACR + HCHO + HO_2	2.00E-12	0	0
MACRO2 + MACRO2	HACET + MGLY + 0.5*HCHO + 0.5*CO + HO_2	2.00E-12	0	0
MeBr + Cl	Br + HCl	1.40E-11	0	1030
MeBr + $O(^1D)$	Br + OH	1.80E-10	0	0
MeBr + OH	Br + H_2O	2.35E-12	0	1300
MeCO3 + NO	MeOO + CO_2 + NO_2	7.50E-12	0	-290
MeCO3 + NO_3	MeOO + CO_2 + NO_2	4.00E-12	0	0
$MeCOCH_2OO$ + NO	MeCO3 + HCHO + NO_2	2.70E-12	0	-360
$MeCOCH_2OO$ + NO_3	MeCO3 + HCHO + NO_2	2.30E-12	0	0
MeOO + NO	HO_2 + HCHO + NO_2	2.30E-12	0	-360
MeOO + MeOO†	HO_2 + HO_2 + HCHO + HCHO	1.03E-13	0	-365
MeOO + MeCO3	HO_2 + HCHO + MeOO	1.80E-12	0	-500
MeOO + MeCO3	MeCO2H + HCHO	2.00E-13	0	-500
MeOO + MeOO†	MeOH + HCHO	1.03E-13	0	-365
MeOO + NO	$MeONO_2$	2.30E-15	0	-360
MeOO + NO_3	HO_2 + HCHO + NO_2	1.20E-12	0	0
N + NO	N_2 + $O(^3P)$	2.10E-11	0	-100
N + NO_2	N_2O + $O(^3P)$	5.80E-12	0	-220
N + O_2	NO + $O(^3P)$	1.50E-11	0	3600
n-PrOO + NO	EtCHO + HO_2 + NO_2	2.90E-12	0	-350

n-PrOO + NO_3	EtCHO + HO_2 + NO_2	2.70E-12	0	-360
N_2O_5 + H_2O	$HONO_2$ + $HONO_2$	2.50E-22	0	0
NO + NO_3	NO_2 + NO_2	1.50E-11	0	-170
NO + O_3	NO_2	3.00E-12	0	1500
NO + ISO2	ISON	1.12E-13	0	-360
NO + ISO2	NO_2 + MACR + HCHO + HO_2	2.43E-12	0	-360
NO + MACRO2	NO_2 + 0.25*MeCO3 + 0.25*HACET + 0.25*CO + 0.5*MGLY + 0.75*HCHO + 0.75*HO_2	2.54E-12	0	-360
NO_2 + NO_3	NO + NO_2 + O_2	4.50E-14	0	1260
NO_2 + O_3	NO_3	1.20E-13	0	2450
NO_3 + Br	BrO + NO_2	1.60E-11	0	0
NO_3 + HCHO	$HONO_2$ + HO_2 + CO	2.00E-12	0	2440
NO_3 + C_5H_8	ISON	3.15E-12	0	450
NO_3 + EtCHO	$HONO_2$ + EtCO3	6.30E-15	0	0
NO_3 + MGLY	MeCO3 + CO + $HONO_2$	3.36E-12	0	1860
NO_3 + Me2CO	$HONO_2$ + $MeCOCH_2OO$	3.00E-17	0	0
NO_3 + MeCHO	$HONO_2$ + MeCO3	1.40E-12	0	1860
$O(^1D)$ + CH_4	HCHO + H_2	9.00E-12	0	0
$O(^1D)$ + CH_4	OH + MeOO	1.31E-10	0	0
$O(^1D)$ + CO_2	$O(^3P)$ + CO_2	7.50E-11	0	-115
$O(^1D)$ + H_2	OH + H	1.20E-10	0	0
$O(^1D)$ + H_2O	OH + OH	1.63E-10	0	-60
$O(^1D)$ + HBr	HBr + $O(^3P)$	3.00E-11	0	0
$O(^1D)$ + HBr	OH + Br	1.20E-10	0	0
$O(^1D)$ + HCl	H + ClO	3.60E-11	0	0
$O(^1D)$ + HCl	$O(^3P)$ + HCl	1.35E-11	0	0
$O(^1D)$ + HCl	OH + Cl	1.01E-10	0	0

$O(^1D) + N_2$	$O(^3P) + N_2$	2.15E-11	0	-110
$O(^1D) + N_2O$	$N_2 + O_2$	4.60E-11	0	-20
$O(^1D) + N_2O$	NO + NO	7.30E-11	0	-20
$O(^1D) + O_2$	$O(^3P) + O_2$	3.30E-11	0	-55
$O(^1D) + O_3$	$O_2 + O(^3P) + O(^3P)$	1.20E-10	0	0
$O(^1D) + O_3$	$O_2 + O_2$	1.20E-10	0	0
$O(^1D) + CH_4$	$HCHO + HO_2 + HO_2$	3.45E-11	0	0
$O(^3P) + BrO$	$O_2 + Br$	1.90E-11	0	-230
$O(^3P) + ClO$	$Cl + O_2$	2.80E-11	0	-85
$O(^3P) + ClONO_2$	$ClO + NO_3$	3.60E-12	0	840
$O(^3P) + H_2$	OH + H	9.00E-18	0	0
$O(^3P) + H_2O_2$	$OH + HO_2$	1.40E-12	0	2000
$O(^3P) + HBr$	OH + Br	5.80E-12	0	1500
$O(^3P) + HCHO$	$OH + CO + HO_2$	3.40E-11	0	1600
$O(^3P) + HCl$	OH + Cl	1.00E-11	0	3300
$O(^3P) + HO_2$	$OH + O_2$	2.70E-11	0	-224
$O(^3P) + HOCl$	OH + ClO	1.70E-13	0	0
$O(^3P) + NO_2$	$NO + O_2$	5.10E-12	0	-210
$O(^3P) + NO_3$	$O_2 + NO_2$	1.70E-11	0	0
$O(^3P) + O_3$	$O_2 + O_2$	8.00E-12	0	2060
$O(^3P) + OClO$	$O_2 + ClO$	2.40E-12	0	960
$O(^3P) + OH$	$O_2 + H$	1.80E-11	0	-180
$O_3 + C_5H_8$	$0.25*HO_2 + 0.25*OH + 0.65*MACR + 0.58*HCHO + 0.1*MACRO2 + 0.1*MeCO3 + 0.08*MeOO + 0.28*HCOOH + 0.14*CO + 0.09*H_2O_2$	9.99E-15	0	1995
$O_3 + MACR$	$0.9*MGLY + 0.45*HCOOH + 0.32*HO_2 + 0.22*CO + 0.19*OH + 0.1*MeCO3$	4.26E-16	0	1520

O_3 + MACR	0.9*MGLY + 0.45*HCOOH + 0.32*HO_2 + 0.22*CO + 0.19*OH + 0.1*MeCO3	7.00E-16	0	2100
OClO + NO	NO_2 + ClO	2.50E-12	0	600
OH + CH_4	H_2O + MeOO	2.45E-12	0	1775
OH + CO†	H + CO_2	1.44E-13	0	0
OH + ClO	HCl + O_2	6.00E-13	0	-230
OH + ClO	HO_2 + Cl	7.40E-12	0	-270
OH + $ClONO_2$	HOCl + NO_3	1.20E-12	0	330
OH + H_2	H_2O + H	2.80E-12	0	1800
OH + HBr	H_2O + Br	5.50E-12	0	-200
OH + HCHO	H_2O + HO_2 + CO	5.40E-12	0	-135
OH + HCl	H_2O + Cl	1.80E-12	0	250
OH + HO_2	H_2O + O_2	4.80E-11	0	-250
OH + H_2O_2	HO_2 + H_2O	2.90E-12	0	160
OH + HO_2NO_2	H_2O + NO_2 + O_2	3.20E-13	0	-690
OH + HOCl	ClO + H_2O	3.00E-12	0	500
OH + $HONO_2$†	H_2O + NO_3	2.40E-14	0	-460
OH + MeOOH	H_2O + MeOO	1.89E-12	0	-190
OH + NO_3	HO_2 + NO_2	2.20E-11	0	0
OH + O_3	HO_2 + O_2	1.70E-12	0	940
OH + OClO	HOCl + O_2	1.40E-12	0	-600
OH + OH	H_2O + $O(^3P)$	6.31E-14	2.6	-945
OH + C_2H_6	H_2O + EtOO	6.90E-12	0	1000
OH + C_3H_8†	i-PrOO + H_2O	7.60E-12	0	585
OH + C_3H_8†	n-PrOO + H_2O	7.60E-12	0	585
OH + C_5H_8	ISO2	2.70E-11	0	-390
OH + EtCHO	H_2O + EtCO3	4.90E-12	0	-405

OH + EtOOH	H_2O + EtOO	1.90E-12	0	-190
OH + EtOOH	H_2O + MeCHO + OH	8.01E-12	0	0
OH + HACET	MGLY + HO_2	1.60E-12	0	-305
OH + HCOOH	HO_2	4.50E-13	0	0
OH + HONO	H_2O + NO_2	2.50E-12	0	-260
OH + ISON	HACET + NALD	1.30E-11	0	0
OH + ISOOH	MACR + OH	1.00E-10	0	0
OH + MACR	MACRO2	1.30E-12	0	-610
OH + MACR	MACRO2	4.00E-12	0	-380
OH + MACROOH	MACRO2	3.77E-11	0	0
OH + MGLY	MeCO3 + CO	1.90E-12	0	-575
OH + MPAN	HACET + NO_2	2.90E-11	0	0
OH + Me2CO	H_2O + $MeCOCH_2OO$	1.70E-14	0	-423
OH + Me2CO	H_2O + $MeCOCH_2OO$	8.80E-12	0	1320
OH + MeCHO	H_2O + MeCO3	4.70E-12	0	-345
OH + MeCO2H	MeOO	8.00E-13	0	0
OH + MeCO3H	MeCO3	3.70E-12	0	0
OH + MeCOCH2OOH	H_2O + $MeCOCH_2OO$	1.90E-12	0	-190
OH + MeCOCH2OOH	OH + MGLY	8.39E-12	0	0
OH + MeOH	HO_2 + HCHO	2.85E-12	0	345
OH + $MeONO_2$	HCHO + NO_2 + H_2O	4.00E-13	0	845
OH + MeOOH	H_2O + HCHO + OH	2.12E-12	0	-190
OH + NALD	HCHO + CO + NO_2	4.70E-12	0	-345
OH + PAN	HCHO + NO_2 + H_2O	3.00E-14	0	0
OH + PPAN	MeCHO + NO_2 + H_2O	1.27E-12	0	0
OH + i-PrOOH	Me2CO + OH	1.66E-11	0	0
OH + i-PrOOH	i-PrOO + H_2O	1.90E-12	0	-190

OH + n-PrOOH	EtCHO + H_2O + OH	1.10E-11	0	0
OH + n-PrOOH	n-PrOO + H_2O	1.90E-12	0	-190
DMS + OH	SO_2	1.20E-11	0	260
DMS + OH	MSA + SO_2	3.04E-12	0	-350
DMS + NO_3	SO_2	1.90E-13	0	-500
DMS + O(^{3}P)	SO_2	1.30E-11	0	-410
COS + O(^{3}P)	CO + SO_2	2.10E-11	0	2200
COS + OH	CO_2 + SO_2	1.10E-13	0	1200
SO_2 + O_3	SO_3	3.00E-12	0	7000
SO_3 + H_2O	H_2SO_4 + H_2O	8.50E-41	0	-6540
Monoterp + OH	0.13*Sec_Org	1.20E-11	0	-444
Monoterp + O_3	0.13*Sec_Org	1.01E-15	0	732
Monoterp + NO_3	0.13*Sec_Org	1.19E-12	0	-925

Table S2: Termolecular reactions used in UKCA StratTrop as implemented in UKESM1.

Reactants	Products	Fc	k_1	α_1	β_1	k_2	α_2	β_2
$O(^3P) + O_2$	O_3	0.00	6.00E-34	-2.5	0	0.00E+00	0	0
$O(^3P) + NO$	NO_2	0.60	9.00E-32	-1.5	0	3.00E-11	0	0
$O(^3P) + NO_2$	NO_3	0.60	2.50E-31	-1.8	0	2.20E-11	-0.7	0
$O(^1D) + N_2$	N_2O	0.00	2.80E-36	-0.9	0	0.00E+00	0	0
$BrO + NO_2$	$BrONO_2$	0.60	5.20E-31	-3.2	0	6.90E-12	0	0
$ClO + ClO$	Cl_2O_2	0.60	1.60E-32	-4.5	0	3.00E-12	-2	0
Cl_2O_2	$ClO + ClO$	0.45	3.70E-07	0.0	7690	1.80E+14	0	7690
$ClO + NO_2$	$ClONO_2$	0.60	1.80E-31	-3.4	0	1.50E-11	0	0
$H + O_2$	HO_2	0.60	4.40E-32	-1.3	0	7.50E-11	0	0
$HO_2 + HO_2$[†]	$H_2O_2 + O_2$	0.00	2.10E-33	0.0	-920	0.00E+00	0	0
$HO_2 + NO_2$	HO_2NO_2	0.60	2.00E-31	-3.4	0	2.90E-12	0	0
HO_2NO_2	$HO_2 + NO_2$	0.50	4.10E-05	0.0	10650	4.80E+15	0	11170
$OH + NO$	$HONO$	0.60	7.00E-31	-2.6	0	3.60E-11	-0.1	0
$OH + NO_2$	$HONO_2$	0.60	1.80E-30	-3.0	0	2.80E-11	0	0
$OH + OH$	H_2O_2	0.60	6.90E-31	-1.0	0	2.60E-11	0	0
$MeCO_3 + NO_2$	PAN	0.30	2.70E-28	-7.1	0	1.20E-11	-0.9	0
PAN	$MeCO3 + NO_2$	0.30	4.90E-03	0.0	12100	5.40E+16	0	13830
$EtCO3 + NO_2$	PPAN	0.30	2.70E-28	-7.1	0	1.20E-11	-0.9	0
PPAN	$EtCO3 + NO_2$	0.30	4.90E-03	0.0	12100	5.40E+16	0	13830
$MACRO2 + NO_2$	MPAN	0.30	2.70E-28	-7.1	0	1.20E-11	-0.9	0
MPAN	$MACRO2 + NO_2$	0.30	4.90E-03	0.0	12100	5.40E+16	0	13830
$NO_2 + NO_3$	N_2O_5	0.35	3.60E-30	-4.1	0	1.90E-12	0.2	0
$N_2O_5 + M$	$NO_2 + NO_3$	0.35	1.30E-03	-3.5	11000	9.70E+14	0.1	11080
$NO + NO$	$NO_2 + NO_2$	0.00	3.30E-39	0.0	-530	0.00E+00	0	0
$SO_2 + OH$	$SO_3 + HO_2$	0.60	3.00E-31	-3.3	0	1.50E-12	0	0

$$k_0 = k_1 \times (T/300)^{\alpha_1} \times \exp(-\beta_1/T)$$

$$k_\infty = k_2 \times (T/300)^{\alpha_2} \times \exp(-\beta_2/T)$$

$$k_{([M],T)} = \left(\frac{k_0[M]}{1 + \frac{k_0[M]}{k_\infty}}\right) F_c^{\left\{1+\left[log_{10}\left(\frac{k_0[M]}{k_\infty}\right)\right]^2\right\}^{-1}}$$

[†]Indicates that extra code is used to account for water dependence of this reaction.

M is used to represent a third body (calculated from the grid box pressure and temperature).

Table S3. Photodissociation reactions used in UKCA-StratTrop. For details of the cross-section and quantum yield information please see Telford et al. (2013).

Reactants	Products
BrCl + hv	Br + Cl
BrO + hv	Br + $O(^3P)$
$BrONO_2$ + hv	Br + NO_3
$BrONO_2$ + hv	BrO + NO_2
CF_2Cl_2 + hv	Cl + Cl
$CFCl_3$ + hv	Cl + Cl + Cl
CH_4 + hv	MeOO + H
Cl_2O_2 + hv	Cl + Cl + O_2
$ClONO_2$ + hv	Cl + NO_3
$ClONO_2$ + hv	ClO + NO_2
CO_2 + hv	CO + $O(^3P)$
COS + hv	CO + SO_2
EtCHO + hv	EtOO + HO_2+ CO
EtOOH + hv	MeCHO + HO_2 + OH
H_2O + hv	OH + H
H_2O_2 + hv	OH + OH
H_2SO_4 + hv	SO_3 + OH
HACET + hv	$MeCO_3$ + HCHO + HO_2
HCHO + hv	HO_2 + HO_2 + CO
HCHO + hv	H_2 + CO
HCl + hv	H + Cl
HO_2NO_2 + hv	HO_2 + NO_2
HO_2NO_2 + hv	OH + NO_3
HOBr + hv	OH + Br

HOCl + hv	OH + Cl
HONO + hv	OH + NO
$HONO_2$ + hv	OH + NO_2
i-PrOOH + hv	Me2CO + HO_2 + OH
ISON + hv	NO_2 + MACR + HCHO + HO_2
ISOOH + hv	OH + MACR + HCHO + HO_2
MACR + hv	MeCO3 + HCHO + CO + HO_2
MACROOH + hv	OH + HO_2 + OH + HO_2
MACROOH + hv	HACET + CO + MGLY + HCHO
Me2CO + hv	MeCO3 + MeOO
MeBr + hv	Br + H
MeCHO + hv	MeOO + HO_2 + CO
MeCHO + hv	CH_4+ CO
MeCO3H + hv	MeOO + OH
$MeCOCH_2OOH$ + hv	MeCO3 + HCHO + OH
$MeONO_2$ + hv	HO_2 + HCHO + NO_2
MeOOH + hv	HO_2 + HCHO + OH
MGLY + hv	MeCO3 + CO + HO_2
MPAN + hv	MACRO2 + NO_2
N_2O + hv	N_2 + $O(^1D)$
N_2O_5 + hv	NO_2 + NO_3
NALD + hv	HCHO + CO + NO_2 + HO_2
NO + hv	N + $O(^3P)$
NO_2 + hv	NO + $O(^3P)$
NO_3 + hv	NO + O_2

NO_3 + hv	NO_2 + $O(^3P)$
n-PrOOH + hv	EtCHO + HO_2 + OH
O_2 + hv	$O(^3P)$ + $O(^3P)$
O_2 + hv	$O(^3P)$ + $O(^1D)$
O_3 + hv	O_2 + $O(^1D)$
O_3 + hv	O_2 + $O(^3P)$
OClO + hv	$O(^3P)$ + ClO
PAN + hv	MeCO3 + NO_2
PPAN + hv	$EtCO_3$ + NO_2
SO_3 + hv	SO_2 + $O(^3P)$

Table S4. Heterogeneous reaction list used in UKCA StratTrop in UKESM1. Uptake coefficients are denoted *f* when not constant; see Denison et al. (2018) for full references and formulation.

Reactants	Products	Uptake coefficient (γ)		
		Liquid aerosol	Nat	Ice
$ClONO_2$ + HCl	Cl + Cl + $HONO_2$	*f*	0.3	0.3
$ClONO_2$ + H_2O	HOCl + $HONO_2$		0.006	0.3
N_2O_5 + H_2O	$HONO_2$ + $HONO_2$	0.1	0.0006	0.03
N_2O_5 + HCl	Cl + NO_2 + $HONO_2$		0.003	0.03
HOCl + HCl	Cl + Cl + H_2O	*f*	0.3	0.3

Table S5. Aqueous phase sulfur cycle reactions used in UKCA StratTrop in UKESM1 (after Kreidenweis et al (2003)).

Reactants	Products	Rate expression /cm^3 $molecule^{-1}$ s^{-1}
$HSO_3^-_{(aq)}$ + $H_2O_{2(aq)}$	$SO_4^{2-}_{(aq)}$	2.1295E+14*exp(-4430.0/T)*([H^+]/(1.0 + 13.0*[H^+]))
$HSO_3^-_{(aq)}$ + $O_{3(aq)}$	$SO_4^{2-}_{(aq)}$	4.0113E+13*exp(-5530.0/T)
$SO_3^{2-}_{(aq)}$ + $O_{3(aq)}$	$SO_4^{2-}_{(aq)}$	7.43E+16*exp(-5280.0/T)

[H^+] is prescribed in UKCA StratTrop in UKESM1 at 1E-5 molecules cm^{-3}.

Table S6. Values required to calculate the effective Henry's Law coefficient for the soluble tropospheric species included in the UKCA strat-trop scheme, where Me=CH_3, Et=C_2H_5, Pr=C_3H_7.

	Henry's Law Data		Dissociation Data	
Species	K_H(298 K)	-$\Delta H/R$	K_a(298 K)	-$\Delta H/R$
	M atm^{-1}	K^{-1}	M	K^{-1}
NO_3	2.0E+00	2000.0	0.0E+00	0.0
N_2O_5	2.1E+05	8700.0	2.0E+01	0.0
HO_2NO_2	1.3E+04	6900.0	1.0E-05	0.0
$HONO_2$	2.1E+05	8700.0	2.0E+01	0.0
HO_2	4.0E+03	5900.0	2.0E-05	0.0
H_2O_2	8.3E+04	7400.0	2.4E-12	-3730.0
HCHO	3.3E+03	6500.0	0.0E+00	0.0
MeOO	2.0E+03	6600.0	0.0E+00	0.0
MeOOH	3.1E+02	5000.0	0.0E+00	0.0
HONO	5.0E+01	4900.0	5.6E-04	-1260.0
EtOOH	3.4E+02	5700.0	0.0E+00	0.0
n-PrOOH	3.4E+02	5700.0	0.0E+00	0.0
i-PrOOH	3.4E+02	5700.0	0.0E+00	0.0
$MeCOCH_2OOH$	3.4E+02	5700.0	0.0E+00	0.0
ISOOH	1.7E+06	9700.0	0.0E+00	0.0

ISON	3.0E+03	7400.0	0.0E+00	0.0
MACROOH	1.7E+06	9700.0	0.0E+00	0.0
HACET	1.4E+02	7200.0	0.0E+00	0.0
MGLY	3.5E+03	7200.0	0.0E+00	0.0
HCOOH	6.9E+03	5600.0	1.8E-04	-1510.0
$MeCO_3H$	7.5E+02	5300.0	6.3E-09	0.0
$MeCO_2H$	4.7E+03	6000.0	1.8E-05	0.0
MeOH	2.3E+02	4900.0	0.0E+00	0.0

Table S7. Values required to calculate the effective Henry's Law coefficient for the soluble stratospheric species included in the UKCA strat-trop scheme, where Me=CH_3, Et=C_2H_5, Pr=C_3H_7.

Species	Henry's Law Data		Dissociation Data	
	K_H(298 K)	-ΔH/R	K_a(298 K)	-ΔH/R
	M atm^{-1}	K^{-1}	M	K^{-1}
$BrONO_2$	2.1E+05	8700.0	1.57E+02	0.0
HCl	1.9E+01	600.0	1.0E+04	0.0
HOCl	9.2E+02	5900.0	3.2E+06	0.0
HBr	1.3E+00	10,200.0	1.0E+09	0.0
HOBr	6.1E+04	0.0	0.0E+00	0.0
$ClONO_2$	2.1E+05	8700.0	1.57E+01	0.0

Table S8. Values required to calculate the effective Henry's Law coefficient for the soluble aerosol precursor species included in the UKCA strat-trop scheme, where Me=CH_3, Et=C_2H_5, Pr=C_3H_7.

Species	Henry's Law Data		Dissociation Data	
	K_H(298 K)	-ΔH/R	K_a(298 K)	-ΔH/R
	M atm^{-1}	K^{-1}	M	K^{-1}
O_3	1.13E-02	2300.0	0.0E+00	0.0
SO_2	1.23E+00	3020.0	1.23E-02	2010.00
DMSO	5.0E+04	6425.0	0.0E+00	0.0

§1.2 One at a time sensitivity experiments.

Table S9: List of experiments performed during the development of the StratTrop scheme. Each experiment was run for 20 years with the last 10 years analysed.

Experiment	Description	O_3 Production (Tg/yr)	O_3 Loss (Tg/yr)	O_3 Net Production (Tg/yr)	STE (inferred) (Tg)	τO_3 (days)	Burden O_3 (Tg)	τCH_4 (years)	Mean [OH] /10^5 cm^{-3}
A	Kinetics: 2005 Photolysis: FJx Emissions: Base ACCMIP Deposition: 2D	5650	4990	661	516 (489)	24.1	411	7.0	11.1
B	Kinetics: 2005; HO_2+NO->$HONO_2$ on. Photolysis: FJx Emissions: Base ACCMIP Deposition: 2D	4920	4410	505	558 (573)	25.3	386	8.0	9.43
C	Kinetics: 2011; HO_2+NO->$HONO_2$ on. Photolysis: FJx Emissions: Base ACCMIP Deposition: 2D	4920	4200	714	334 (299)	23.5	340	7.9	9.35
D	Kinetics: 2005; HO_2+NO->$HONO_2$ on. Photolysis: 2D Emissions: Base ACCMIP Deposition: 2D	3900	3250	649	387 (375)	28.9	343	11.7	6.07
E	Kinetics: 2011; HO_2+NO->$HONO_2$ on. Photolysis: FJx Emissions: Base ACCMIP Deposition: Wesley	4850	4200	653	349 (369)	22.8	330	7.7	9.56

F	Kinetics: 2011; HO_2+NO->$HONO_2$ on. Photolysis: FJx Emissions: Base ACCMIP + interactive CH_4 Deposition: Wesley	4630	4180	456	304 (513)	21.1	302	8.0	9.25
G	Kinetics: 2011; HO_2+NO->$HONO_2$ on. Photolysis: FJx Emissions: Base ACCMIP + Biogenic MeOH Deposition: Wesley	5000	4330	679	354 (363)	23.0	343	7.5	9.81
H	Kinetics: 2011; HO_2+NO->$HONO_2$ on. Photolysis: FJx Emissions: Base ACCMIP + Biogenic MeOH Deposition: Wesley Radiation: Non-interactive ozone.	5000	4360	634	412 (421)	23.0	347	7.5	9.81
I	Kinetics: 2011; HO_2+NO->$HONO_2$ on. Photolysis: FJx Emissions: Base ACCMIP + Biogenic MeOH Deposition: Wesley Chemistry: LLSF Isoprene (Squire et al., 2015)	4850	4140	708	351 (304)	23.2	333	7.77	9.52

J	Kinetics: 2011; HO_2+NO->$HONO_2$ on. Photolysis: FJx Emissions: Base ACCMIP + Biogenic MeOH Deposition: Wesley Chemistry: CheT2 Isoprene (Squire et al., 2015)	4830	4120	707	351 (305)	23.1	330	7.71	9.63
K	Kinetics: 2011; HO_2+NO->$HONO_2$ on. Photolysis: FJx Emissions: Base ACCMIP + Biogenic MeOH + 2*Isoprene Deposition: Wesley Chemistry: LLSF Isoprene (Squire et al., 2015)	5270	4560	718	337 (388)	22.5	350	8.65	8.39
L	Kinetics: 2011; HO_2+NO->$HONO_2$ on. Photolysis: FJx Emissions: Base ACCMIP + Biogenic MeOH + 0.5*Isoprene Deposition: Wesley Chemistry: LLSF Isoprene (Squire et al., 2015)	4470	3800	664	300 (336)	23.3	309	7.33	10.2

M	Kinetics: 2011; HO_2+NO->$HONO_2$ on. Photolysis: FJx Emissions: Base ACCMIP + Biogenic MeOH + 0.5*LNOx Deposition: Wesley	4460	3820	642	309 (332)	25.8	304	8.77	8.43
N	Kinetics: 2011; HO_2+NO->$HONO_2$ on. Photolysis: FJx Emissions: Base ACCMIP + Biogenic MeOH + 0.5*Soil NOx Deposition: Wesley	4860	4170	682	321 (353)	23.5	338	7.98	9.24
	ACCMIP mean	5230.0	4322.0	908.0		22.3	337±23	9.8±1.6	11.1±1.8

Key: *FJx = Fast-JX photolysis; 2D = same photolysis scheme as used in HadGEM2-ES; Base ACCMIP = year 2000 emissions from Lamarque et al. (2010); Biogenic MeOH = climatology of biogenic MeOH emissions from Stavrakou et al. (2011); Deposition 2D = using the deposition scheme as described in Morgenstern et al. (2009); Deposition Wesley = using the Wesley deposition scheme discussed here; Chemistry LLSF isoprene = using the LLSF isoprene chemical mechanism as discussed in Squire et al. (2015); Chemistry CheT2 isoprene = using the CheT2 isoprene chemical mechanism as discussed in Squire et al. (2015). The values in parenthesise indicate the inferred STE from closure of the ozone budget: S=P-L-D, whereas the diagnosed STE flux is given above these data.*

Output from these simulations has been used to provide a preliminary evaluation of the overall sensitivity of surface O_3, OH, PAN, $HONO_2$, H_2O_2 and HCHO to a number of processes in the model (see Figures S1-S6).

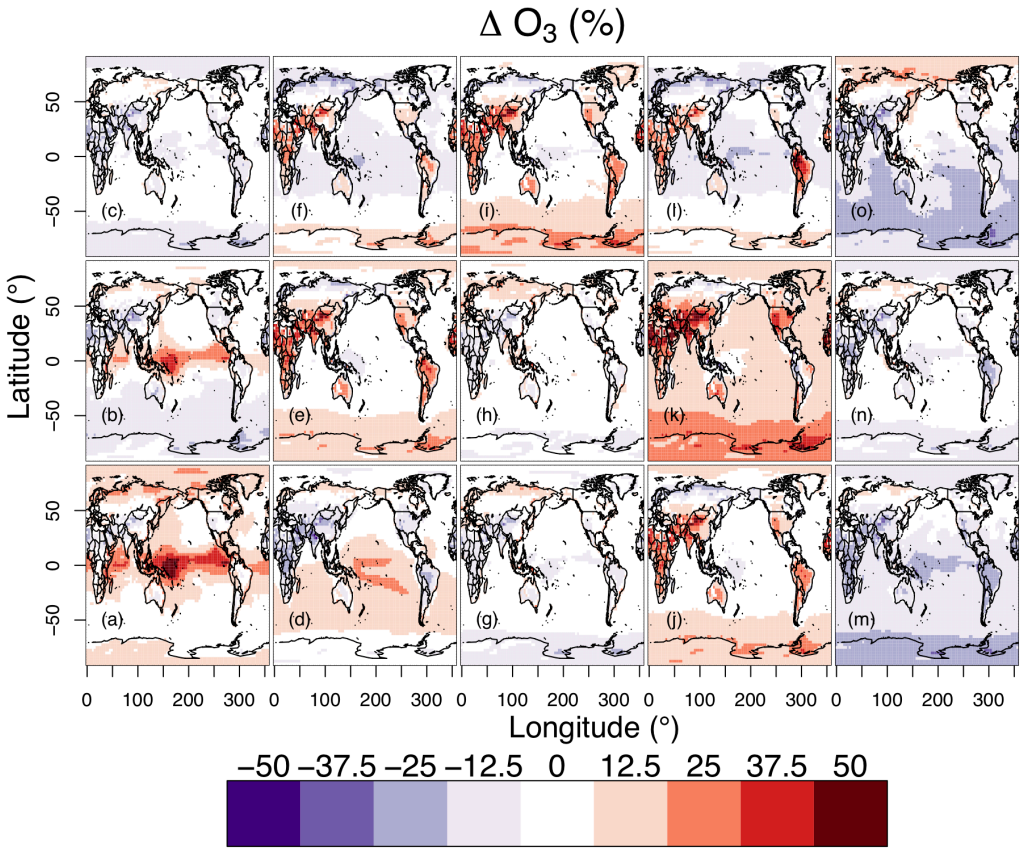

Figure S1: Comparison of changes in annual average surface ozone across the model simulations outlined in Table S9. All model simulations were combined to generate an ensemble mean and the panels show the relative % difference {%((simulation$_i$-ensemble mean)/ensemble mean)} for each simulation to the ensemble mean.

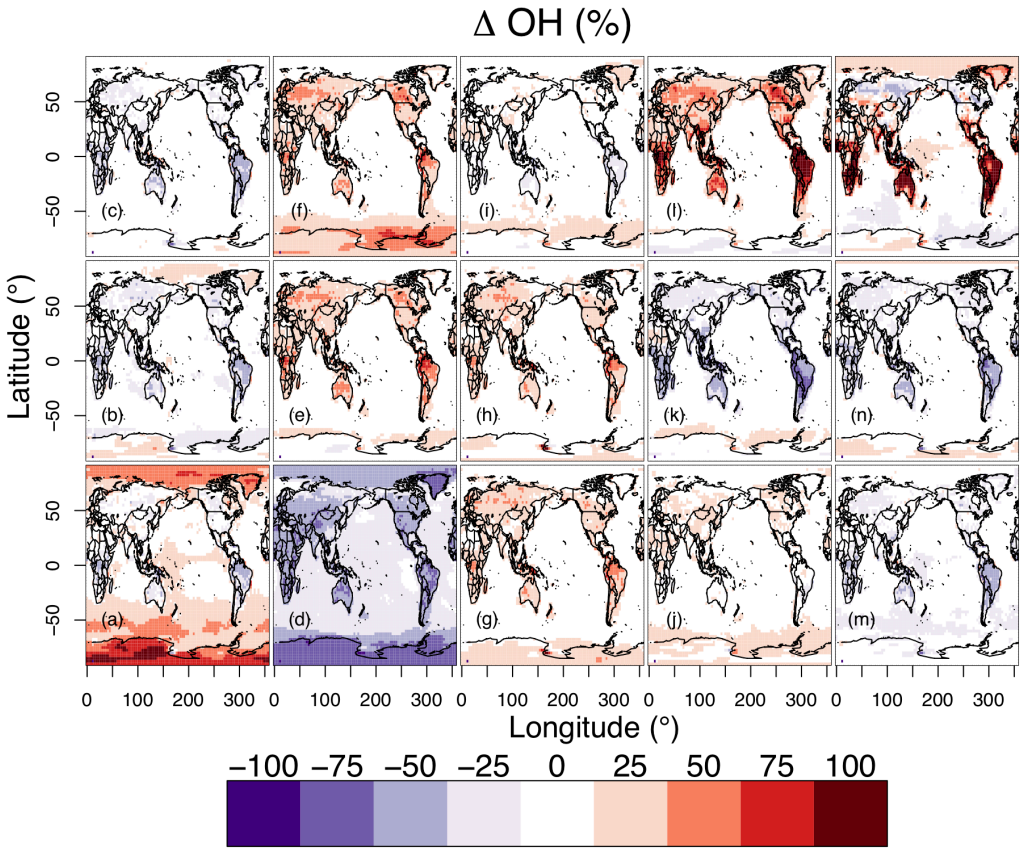

Figure S2: As Figure S1 for surface hydroxyl radical.

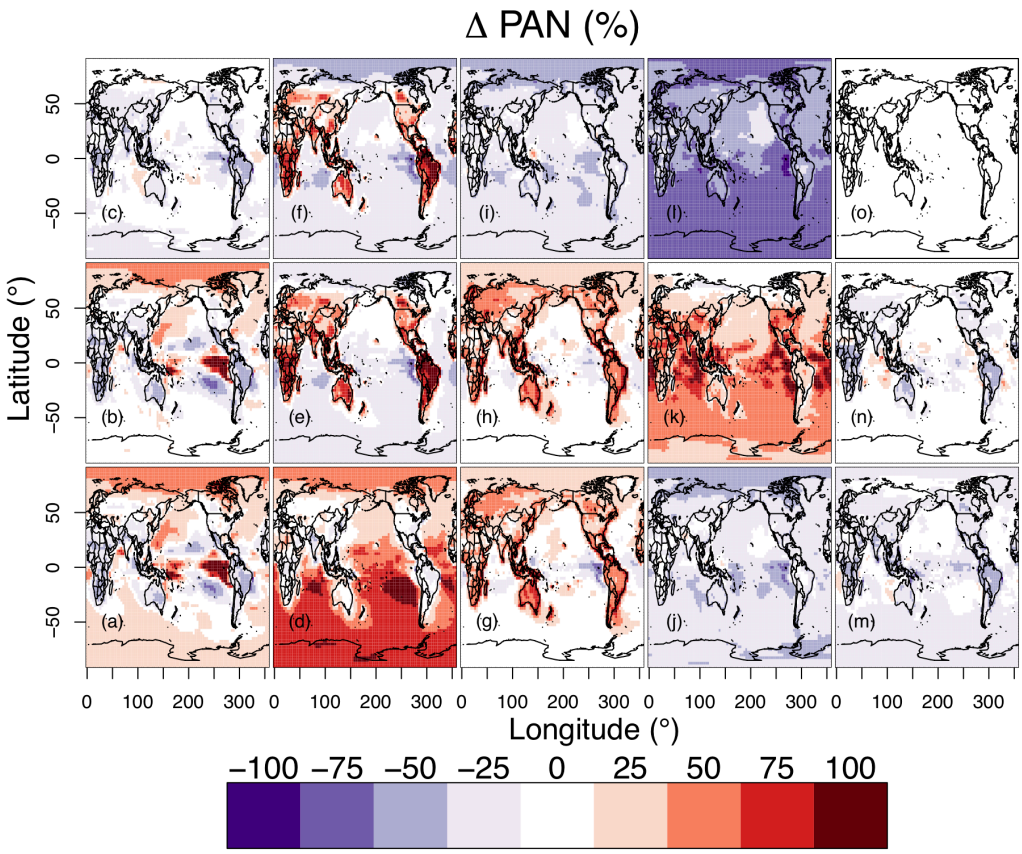

Figure S3: As figure S1 for surface PAN.

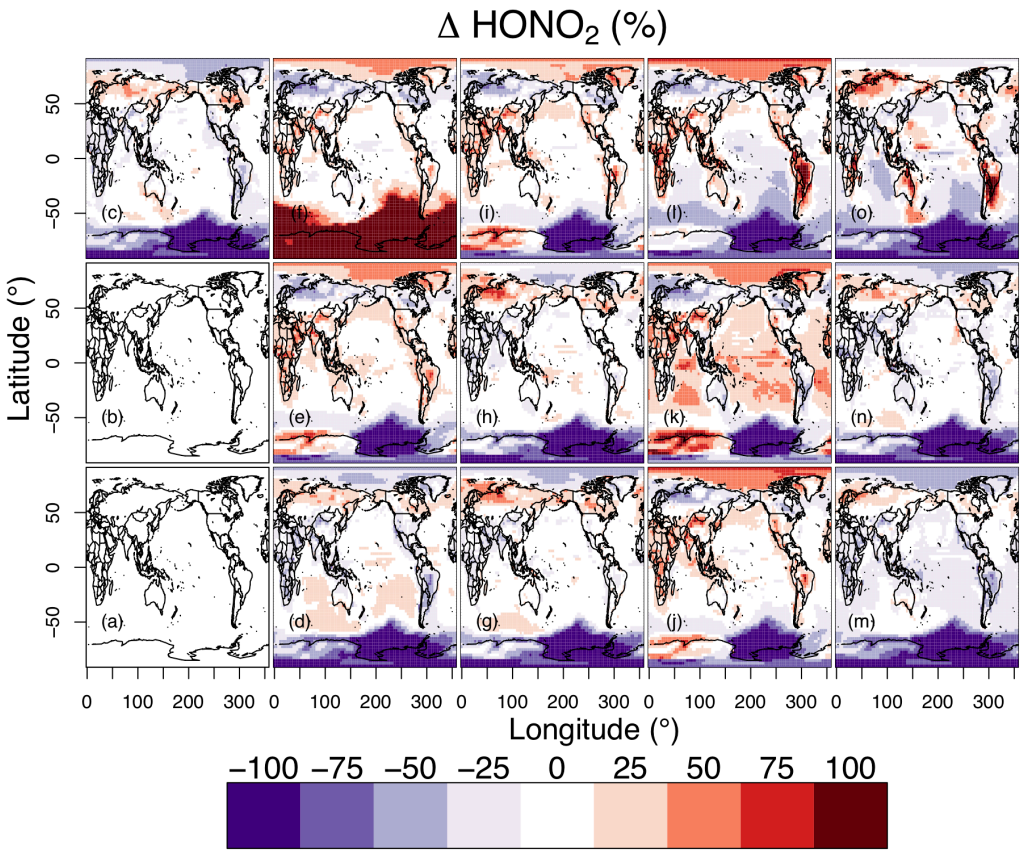

Figure S4: As Figure S1 for surface nitric acid.

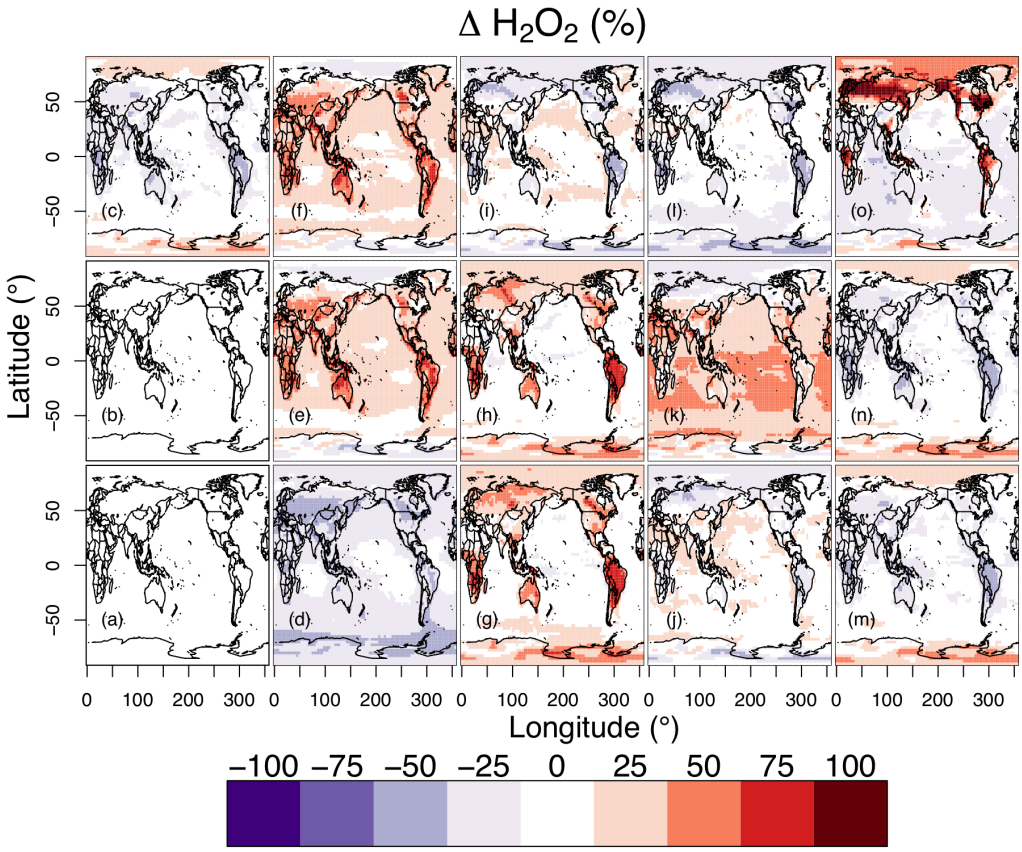

Figure S5: As Figure S1 for surface hydrogen peroxide.

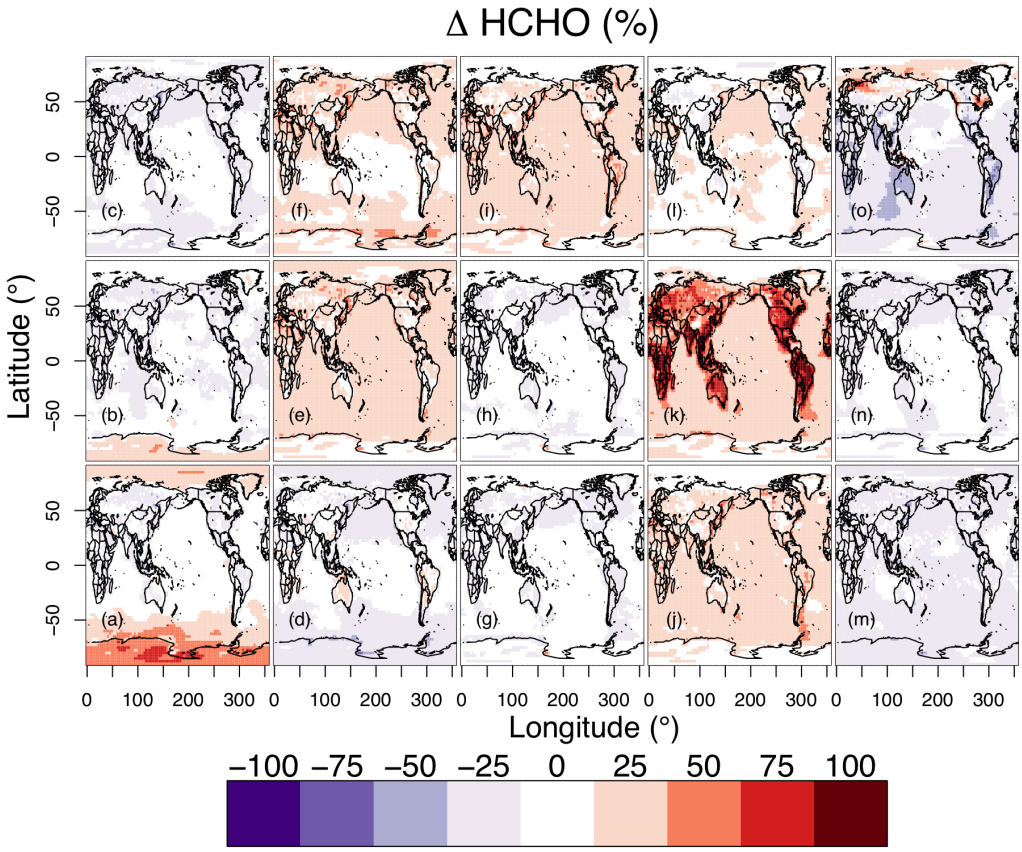

Figure S6: As Figure S1 for surface formaldehyde.

§2.1 Discussion of the emissions used in model evaluation.

Table S10 provides a summary of the sectors contributing to the emissions of the nine tropospheric ozone precursor species treated in UKCA StratTrop and their corresponding global annual totals, averaged over the 2005-2014 time period covered by the two simulations. Figures S7 and S8 show the multi-annual global annual mean distributions and the seasonal cycle for different emission sectors and regions for NO and CO, respectively. While the figures illustrate that the main contribution to NO and CO emissions is of anthropogenic origin, other sectors are relevant in shaping the yearly cycle. Examples include emissions of NO from biomass burning in the tropics, soil NO emissions in the northern extratropics, land biogenic CO emissions in the extratropics and ocean biogenic CO emissions in the southern extratropics.

It is worth noting that the CMIP6 global annual total for anthropogenic NO_x emissions (Hoesly et al., 2018), for example, is higher than that used in the 5th Coupled Model Intercomparison Project (Lamarque et al., 2010) and the Atmospheric Composition and Climate Model Intercomparison Project (ACCMIP; Lamarque et al., 2013). Part of this difference is due to the time period. ACCMIP used decadal mean emissions, centred on the year 2000 for the present-

day whereas here, transient emissions with an annual frequency up to and including the year 2014 are used. With a strong positive trend in anthropogenic emissions shown in Hoesly et al. (2018) since 2000, this difference in time period will be a contributing factor. However, even comparing CMIP5 and CMIP6 anthropogenic emissions (excluding aircraft and agricultural waste burning) for the same time period shows an appreciable difference (Figure 2 in Hoesly et al., 2018), with CMIP6 emissions being approximately 10 % higher than those used in CMIP5. This could have implications for model performance relative to the ACCMIP studies.

Table S10. List of emitted tropospheric ozone precursor species in UKCA StratTrop, including the contributing sectors and the corresponding global annual totals, averaged over the time period of the simulations i.e. 2005-2014 inclusive.

Species	**Sector**	**Total**
NO_x	Anthropogenic (excluding aircraft) Biomass burning Soil Aircraft Lightning **Total (Tg(NO)/year)**	89.4 14.3 11.8 1.9 12.7 **130.1**
CO	Anthropogenic Biomass burning Land biogenic Ocean biogenic **Total (Tg(CO)/year)**	603.3 347.0 88.6 19.6 **1089.5**
HCHO	Anthropogenic Biomass burning Land biogenic **Total (Tg(HCHO)/year)**	2.4 4.8 4.6 **11.8**
C_2H_6 (including C_2H_4)	Anthropogenic Biomass burning Land biogenic Ocean biogenic **Total (Tg(C_2H_6)/year)**	16.3 9.3 31.1 2.4 **59.1**
C_3H_8 (including C_3H_6)	Anthropogenic Biomass burning Land biogenic Ocean biogenic **Total (Tg(C_3H_8)/year)**	10.2 4.5 15.6 2.8 **33.1**
MeCHO (including other aldehydes but *not* HCHO)	Anthropogenic Biomass burning Land biogenic **Total (Tg(MeCHO)/year)**	1.9 7.1 21.5 **30.5**
Me_2CO	Anthropogenic Biomass burning Land biogenic	2.8 3.0 37.4

	Total (Tg(Me_2CO)/year)	**43.2**
MeOH	Anthropogenic Biomass burning Land biogenic **Total (Tg(MeOH)/year)**	3.8 8.1 129.1 **141.0**
C_5H_8	Land biogenic **Total (Tg(C)/year)**	495.9 **495.9**
$C_{10}H_{16}$	Land biogenic **Total (Tg(C)/year)**	115.1 **115.1**

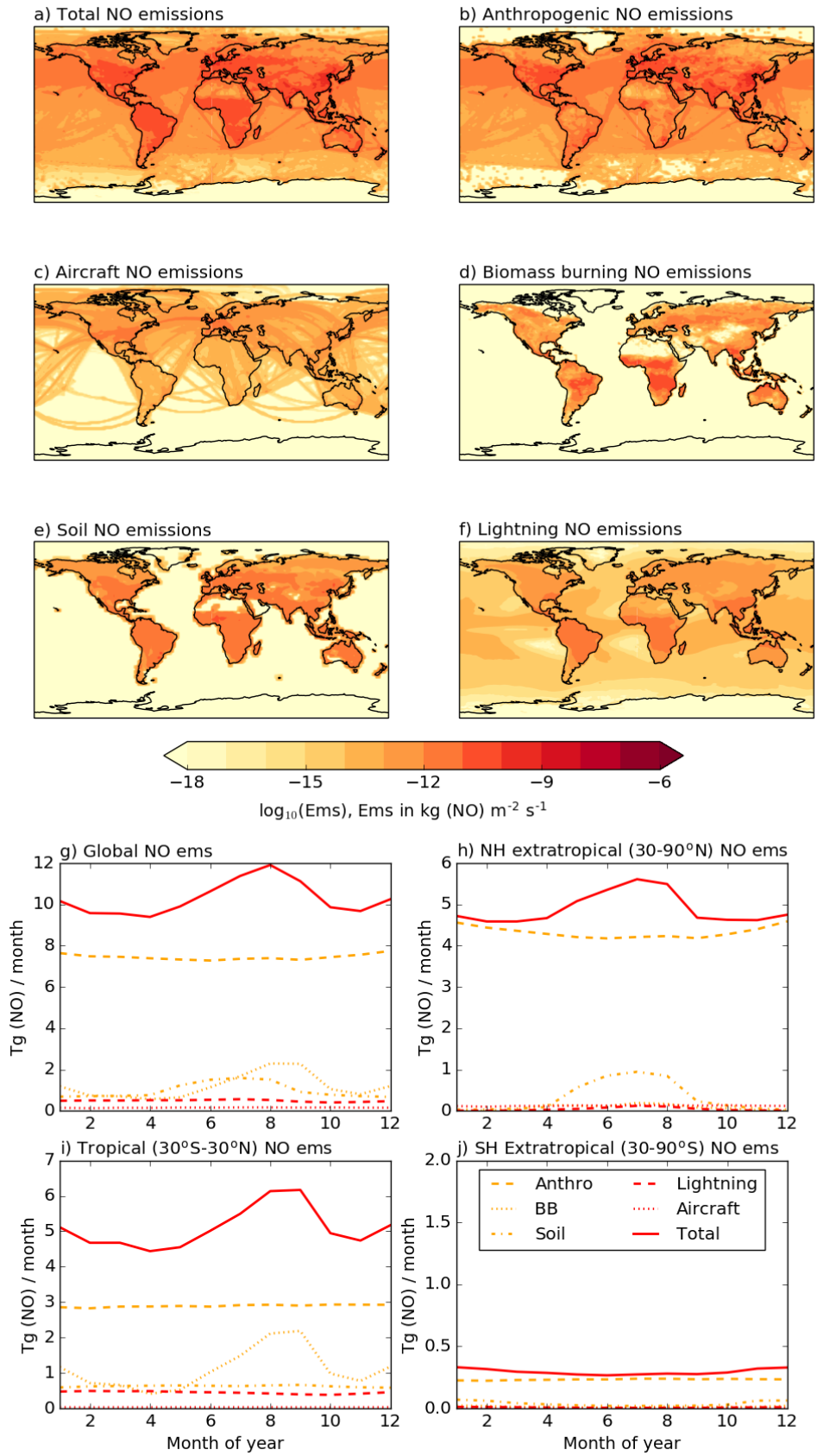

Figure S7. Multi-annual mean NO emissions distribution (plotted as $\log_{10}$(Ems), with Ems in kg (NO) m^{-2} s^{-1}) used in the simulations presented here. Panel (a) highlights the total NO emissions, while panels (b) to (f) show the contributions from anthropogenic, aircraft, biomass burning, soil, and lightning sources, respectively. Aircraft and lightning emissions have been integrated in the vertical. Panels (g)

to (j) show the multi-annual seasonal cycle in Tg(NO)/month over the whole globe, the northern hemisphere (NH) extratropics (30-90°N), the tropics (30°S-30°N), and the southern hemisphere (SH) extratropics (30-90°S), respectively.

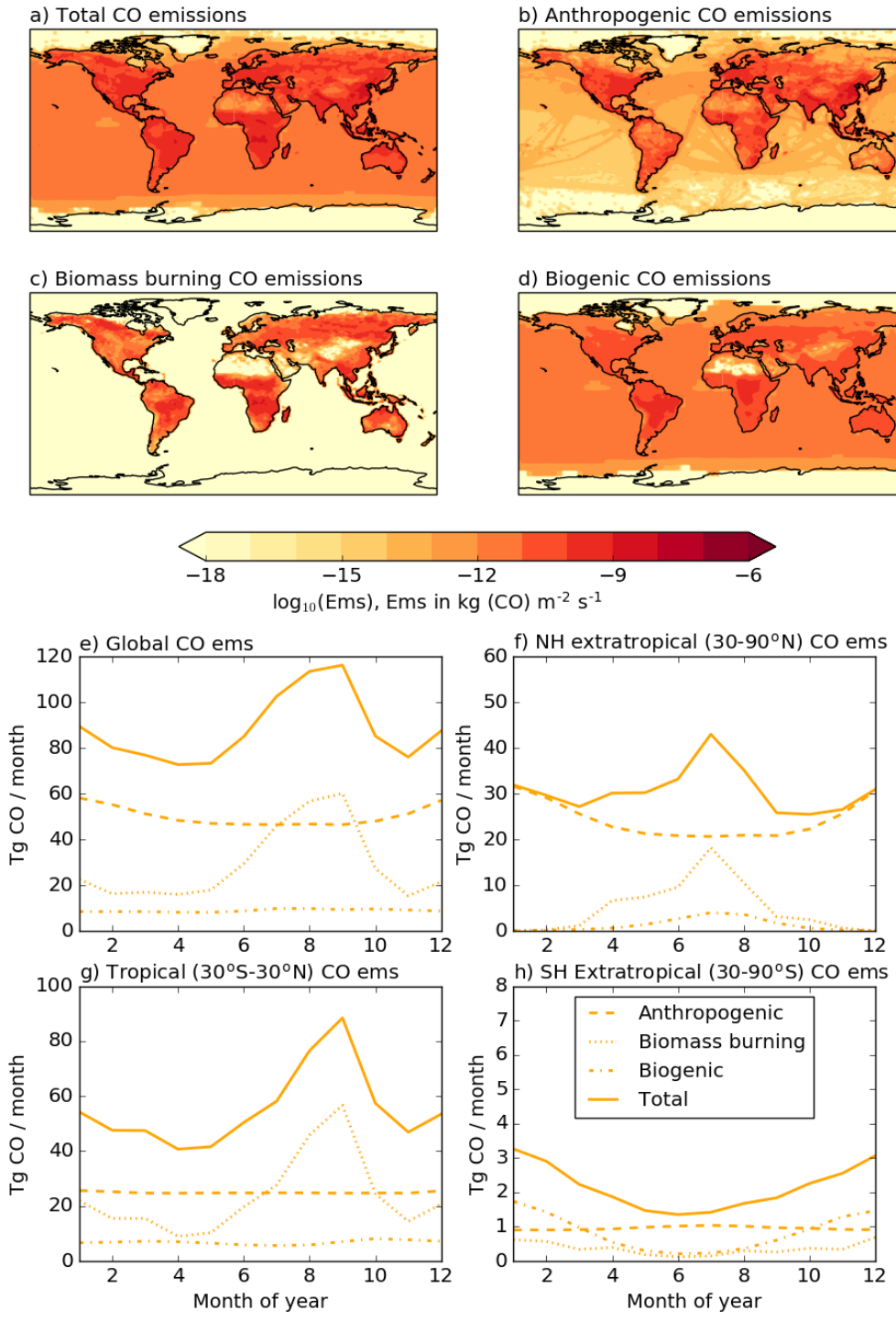

Figure S8. Multi-annual mean CO emissions distribution (plotted as $\log_{10}$(Ems), with Ems in kg (CO) m^{-2} s^{-1}) used in the simulations presented here. Panel (a) highlights the total CO emissions, while panels (b) to (d) show the contributions from anthropogenic, biomass burning and biogenic sources, respectively. Panels (e) to (h) show the multi-annual seasonal cycle in Tg(CO)/month over the whole

globe, the northern hemisphere (NH) extratropics (30-90°N), the tropics (30°S-30°N), and the southern hemisphere (SH) extratropics (30-90°S), respectively.

§2.2 Comparison of model simulated and observed distribution of H_2O_2

Whilst not as important an oxidant as OH or O_3 in the gas phase, H_2O_2 is important for the oxidation of SO_2 in the aqueous phase. Indeed, in our UKCA StratTrop simulations roughly 30% of SO_2 is oxidised by H_2O_2 in the aqueous phase and as such it is important to evaluate the performance of our simulation of H_2O_2. Unlike O_3, there are no satellite products available to give global coverage, or indirect measures of its abundance as in the case for OH with regards to the lifetime of CH_4. As such we rely on in situ observations to make an assessment of model performance.

Figure S9 compares the vertical profiles of the decadal average H_2O_2 mixing ratios from the FR simulation described above in red and in blue one of the older UKCA StratTrop simulations described in Section 2.8 (i.e. Figure 4 blue dots) with observations from a range of aircraft measurement campaigns in grey. This analysis builds on the work of Emmons et al. (2000) and the secondary y axis on each plot (right hand side) indicates the number of observations that make up the observed mean and standard deviation. Each panel in Figure 135 shows the vertical profile of H_2O_2 sampled at different times (monthly averages for the model and periods indicated on the top of the panels for the observations).

The general feature of Figure S9 is that the UKCA StratTrop in UKESM1 simulations tend to result in higher levels of H_2O_2 than in the previous version of UKCA. There is generally good agreement with the observed vertical profile in most locations. The model simulations tend to underestimate the variability shown in the observations. Nevertheless, caution should be applied when assessing the spread of the observations as many of the campaigns had specific foci to target chemical or meteorological events while here they are compared to monthly mean H_2O_2 in the model.

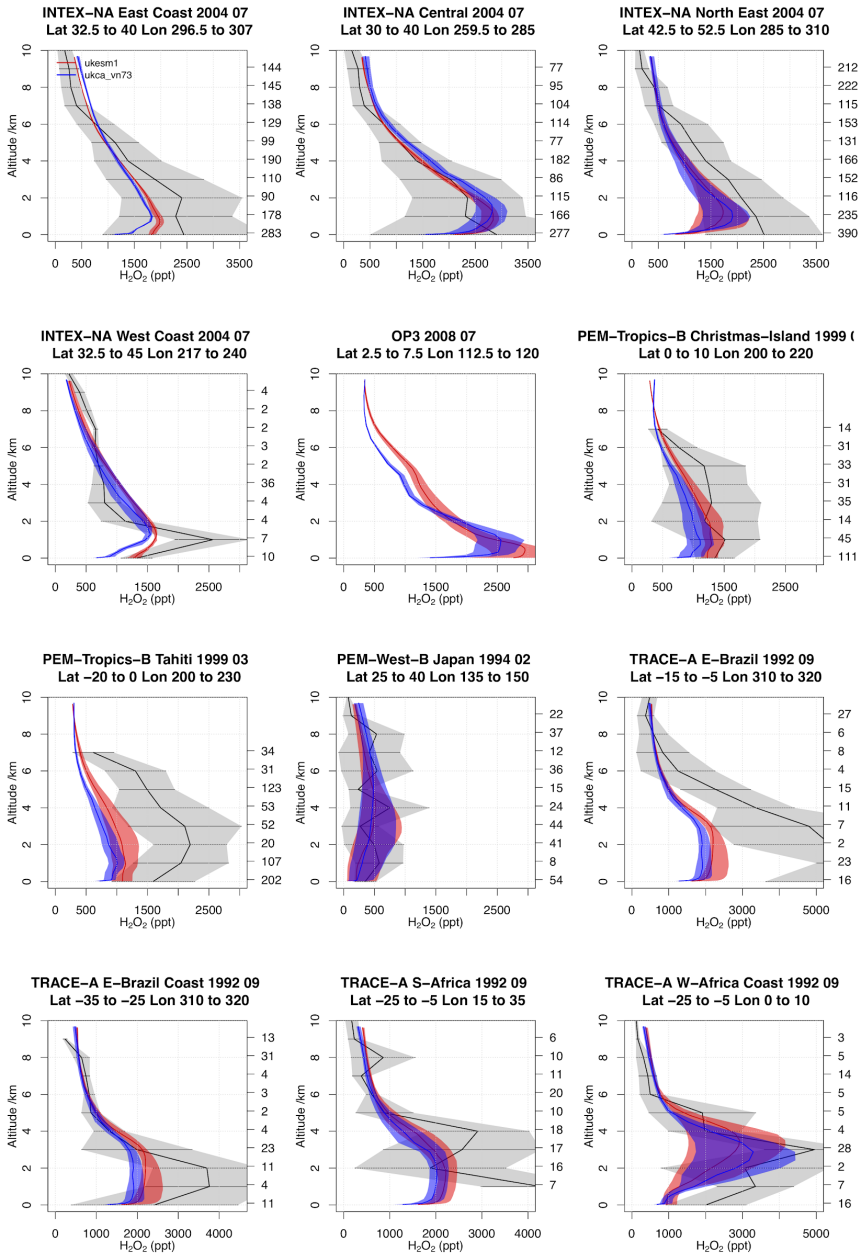

Figure S9. Comparison of modelled (red and blue) H_2O_2 vertical profiles against observations from aircraft campaigns (grey). The red profiles indicate the results from the free running UKCA StratTrop in UKESM1 simulation described here and blue for results from an older UKCA StratTrop simulation running in MetUM vn7.3, (Experiment G, see Supplement for details). All plots show the mean as the solid line and the envelope being ±1 standard deviation.

References

Emmons, L. K., Hauglustaine, D. A., Müller, J.-F., Carroll, M. A., Brasseur, G. P., Brunner, D., Staehelin, J.,Thouret, V., and Marenco, A. (2000), Data composites of airborne observations of tropospheric ozone and its precursors, *J. Geophys. Res.*, 105(D16), 20497– 20538, doi:10.1029/2000JD900232.

Hoesly, R. M., Smith, S. J., Feng, L., Klimont, Z., Janssens-Maenhout, G., Pitkanen, T., Seibert, J. J., Vu, L., Andres, R. J., Bolt, R. M., Bond, T. C., Dawidowski, L., Kholod, N., Kurokawa, J.-I., Li, M., Liu, L., Lu, Z., Moura, M. C. P., O'Rourke, P. R., and Zhang, Q.: Historical (1750–2014) anthropogenic emissions of reactive gases and aerosols from the Community Emissions Data System (CEDS), Geosci. Model Dev., 11, 369-408, https://doi.org/10.5194/gmd-11-369-2018, 2018.

Lamarque, J.-F., Bond, T. C., Eyring, V., Granier, C., Heil, A., Klimont, Z., Lee, D., Liousse, C., Mieville, A., Owen, B., Schultz, M. G., Shindell, D., Smith, S. J., Stehfest, E., Van Aardenne, J., Cooper, O. R., Kainuma, M., Mahowald, N., McConnell, J. R., Naik, V., Riahi, K., and van Vuuren, D. P.: Historical (1850–2000) gridded anthropogenic and biomass burning emissions of reactive gases and aerosols: methodology and application, Atmos. Chem. Phys., 10, 7017–7039, doi:10.5194/acp-10-7017-2010, 2010.

Lamarque, J.-F., Shindell, D. T., Josse, B., Young, P. J., Cionni, I., Eyring, V., Bergmann, D., Cameron-Smith, P., Collins, W. J., Doherty, R., Dalsoren, S., Faluvegi, G., Folberth, G., Ghan, S. J., Horowitz, L. W., Lee, Y. H., MacKenzie, I. A., Nagashima, T., Naik, V., Plummer, D., Righi, M., Rumbold, S. T., Schulz, M., Skeie, R. B., Stevenson, D. S., Strode, S., Sudo, K., Szopa, S., Voulgarakis, A., and Zeng, G.: The Atmospheric Chemistry and Climate Model Intercomparison Project (ACCMIP): overview and description of models, simulations and climate diagnostics, Geosci. Model Dev., 6, 179–206, https://doi.org/10.5194/gmd-6-179-2013, 2013.

Morgenstern, O., Braesicke, P., O'Connor, F. M., Bushell, A. C., Johnson, C. E., Osprey, S. M., and Pyle, J. A.: Evaluation of the new UKCA climate-composition model – Part 1: The stratosphere, Geosci. Model Dev., 2, 43–57, https://doi.org/10.5194/gmd-2-43-2009, 2009.

Squire, O. J., Archibald, A. T., Griffiths, P. T., Jenkin, M. E., Smith, D., and Pyle, J. A.: Influence of isoprene chemical mechanism on modelled changes in tropospheric ozone due to climate and land use over the 21st century, Atmos. Chem. Phys., 15, 5123-5143, https://doi.org/10.5194/acp-15-5123-2015, 2015.

Stavrakou, T., Guenther, A., Razavi, A., Clarisse, L., Clerbaux, C., Coheur, P.-F., Hurtmans, D., Karagulian, F., De Mazière, M., Vigouroux, C., Amelynck, C., Schoon, N., Laffineur, Q., Heinesch, B., Aubinet, M., Rinsland, C., and Müller, J.-F.: First space-based derivation of the global atmospheric methanol emission fluxes, Atmos. Chem. Phys., 11, 4873-4898, https://doi.org/10.5194/acp-11-4873-2011, 2011.

Telford, P. J., Abraham, N. L., Archibald, A. T., Braesicke, P., Dalvi, M., Morgenstern, O., O'Connor, F. M., Richards, N. A. D., and Pyle, J. A.: Implementation of the Fast-JX Photolysis scheme (v6.4) into the UKCA component of the MetUM chemistry-climate model (v7.3), Geosci. Model Dev., 6, 161–177, https://doi.org/10.5194/gmd-6-161-2013, 2013.