



Isoprene chemistry in pristine and polluted Amazon environments

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# Isoprene chemistry in pristine and polluted Amazon environments: Eulerian and Lagrangian model frameworks and the strong bearing they have on our understanding of surface ozone and predictions of rainforest exposure to this priority pollutant

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bons and oxygenated hydrocarbons with a typical cycle time of 3–5 s. Isoprene mixing ratios were determined using a dynamically-diluted calibrated gas standard ( $\sim 500$  ppb in nitrogen, uncertainty  $\pm 5\%$ , Apel-Reimer, Boulder CO). For the purposes of this comparison we have applied a 15-point smoothing function to the high frequency data to give an approximately 1 min moving averaged mixing ratio. The mean limit of detection for isoprene under these conditions was 110 ppt. The overall measurement uncertainty is estimated to be  $\pm 15\%$ . Full instrumental, operational and calibration details are described in Murphy et al. (2010).

Additionally, whole air samples (WAS) were collected on flights B735 and B749, and subsequently analysed to measure isoprene mixing ratios. The WAS system, described in greater detail by Lidster et al. (2014), comprises sixty four canisters with fused silica deactivated inner surfaces, each with three litre internal volume. Individual canisters were filled at operator-determined times using a double-headed metal bellows pump (all stainless steel components) to a final pressure of up to 40 psi and shipped back to the UK for analysis within one month of collection. Analysis was performed using a dual channel gas chromatograph with flame ionisation detectors, described in detail by Hopkins et al. (2011), which was calibrated using a certified standard supplied by the National Physical Laboratory (Ozone precursors mix, cylinder number D641613). Detection limits were in the single parts per trillion range with typical calculated uncertainties of between 3 and 20 %.

## 2.2 UM-UKCA and CiTTyCAT models

### 2.2.1 UM-UKCA (Eulerian model)

We start from the setup of UM-UKCA, employing present day boundary conditions, that Squire et al. (2014) demonstrated had some skill at reproducing recent tropospheric  $O_3$  observations (sonde profiles from the SHADOZ network; see their Fig. 3). This setup, similar to that described by Telford et al. (2010), was comprised of the Hadley Centre Global Environment Model version 3 – Atmosphere only (HadGEM3-A r2.0) at

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UM version 7.3 (Hewitt et al., 2011) and UKCA TropChem (O'Connor et al., 2014). For full details, the reader is referred to Squire et al. (2014). Here, we simply note that the model was run in “climate mode” – at a relatively low spatial resolution, N48 L60 (3.75° longitude × 2.5° latitude; 60 hybrid height levels stretching from the surface to around 84 km) – and employed the standard tropospheric chemistry mechanism, CheT. This is the setup that Squire et al. (2015) subsequently used in their “BASE CheT” experiment. Their “BASE CheT2” experimental setup was identical except for employing the updated CheT2 chemistry. Here, we carry out two integrations with UM-UKCA based on Squire et al. (2015)’s BASE CheT and BASE CheT2 experiments: UM-UKCA (CheT) and UM-UKCA (CheT2), respectively.

Our integrations differ from Squire et al. (2015)’s in four ways: we employ different trace gas emissions, as outlined in Sect. 2.4; we nudge UM-UKCA towards European Centre for Medium-range Weather Forecasts (ECMWF) ERA Interim analyses, as described by Telford et al. (2009); we run the model for just less than 9.5 months (8 months from 00:00 UT 2 January 2012 to spin the model up from BASE CheT and BASE CheT2 start dumps, and a further 40 days from 00:00 UT 2 September 2012 to cover the SAMBBA campaign period); and we output the concentrations of all chemical species at points spaced one minute apart along each of the five SAMBBA flights, using Telford et al. (2013)’s flight track code. Note that we also output the concentrations of all chemical species simulated at the times and locations of the air parcel trajectories 7 days previously, based on the back-trajectory calculations mentioned in Sect. 2.1.1. These data are used to initialise the integrations with CiTTYCAT. Likewise, when modelling the composition of air downwind of Manaus, we provide UM-UKCA with an artificial “flight track” to output the concentrations of chemical species simulated at 6 hourly intervals (throughout September 2012) at a boundary layer site (61.0° W, 3.1° S, 900 hPa) roughly 100 km downwind (1° west) of Manaus, and at the locations of the corresponding air parcels 7 days previously – based on further back-trajectory calculations.

## 2.2.2 CiTTYCAT (Lagrangian model)

CiTtYCAT r4.2.1 (Pugh et al., 2012) is a Lagrangian model of atmospheric chemistry and transport, stemming from the Cambridge Tropospheric Trajectory model of Chemistry And Transport (Wild et al., 1996). This is not the first time that CiTTYCAT has been used to simulate atmospheric chemistry and composition over a tropical rainforest: Pugh et al. (2010), as briefly referred to in the introduction, tested the performance of the model in two-box mode (two boxes, to account for the nocturnal collapse of the boundary layer and development of a residual layer above it), confronting it with measurements made during the OP3 campaign at Danum Valley, Malaysian Borneo. We use the model in single trajectory mode (moving a single model box along one trajectory at a time) many times over as we loop over all back-trajectories bound for (a) the arrival points spaced one minute apart on the five SAMBBA flights, and (b) the receptor site downwind of Manaus at 6 hourly intervals throughout September 2012. The single trajectory mode has been used extensively in previous studies of long range transport (see, e.g., Wild et al., 1996; Evans et al., 2000; Real et al., 2007, 2008). Note that the treatment of transport constitutes the main difference between CiTTYCAT and UM-UKCA: transport in the Lagrangian framework is described by discrete trajectories (series of times and locations) calculated offline, as opposed to fluxes between adjacent model boxes in a fixed 3-D Eulerian grid.

The back-trajectories, illustrated in Fig. 1, are calculated using ROTRAJ (Methven, 1997) in conjunction with ECMWF ERA Interim analyses, as previously outlined by Pugh et al. (2012). The analysed wind fields, available at 6 hourly intervals (00:00 UT, 06:00 UT, 12:00 UT and 18:00 UT) are interpolated linearly in space and time. The location of each trajectory is then calculated by integrating the interpolated wind velocities with respect to time according to the fourth order Runge–Kutta method (Methven, 1997) and recorded every 6 h together with the air temperature and specific humidity, which are also interpolated in space and time from the analyses.

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To ensure the transport in the two models is broadly consistent, we use the same analyses to calculate the trajectories as we use to nudge UM-UKCA (see above). However, two key differences remain. Firstly, the trajectory calculations exploit the full-resolution of the analysed winds (roughly  $0.7^\circ \times 0.7^\circ$ ) whilst UM-UKCA is nudged towards these winds following degradation to the resolution of its Eulerian grid ( $3.75^\circ \times 2.5^\circ$  in “climate mode”). The transport in CiTTYCAT is therefore more finely resolved and should yield greater structure in the composition of air it simulates along each flight track, and downwind of Manaus, particularly when combined with high resolution trace gas emissions. The transport in CiTTYCAT, however, only includes convection as captured by the analyses (i.e. large-scale convection) whilst UM-UKCA explicitly adds updrafts and downdrafts associated with convection on smaller scales, following Gregory and Rowntree (1990) and Gregory and Allen (1991). CiTTYCAT therefore lacks a certain amount of vertical mixing. Some mixing within the boundary layer is included implicitly, as the addition of emissions (conversion from mass fluxes to enhancements in concentration) depends on a length scale associated with the height of the boundary layer, but no ventilation of the boundary layer or exchange with the free troposphere is included. We focus first on the simulation of independent air parcels – with no vertical (or horizontal) mixing – to explore the influence of contrasting air parcel histories on the chemistry ensuing therein. However, we subsequently explore the sensitivity of some of our results to a simple treatment of diffusive vertical mixing.

The treatment of diffusive vertical mixing, described by Pugh et al. (2012), comprises relaxation towards background composition at rates specified by free-troposphere and boundary-layer diffusion coefficients,  $\kappa_{FT}$  and  $\kappa_{BL}$ . These yield relaxation timescales of  $\tau_{FT} = D^2 / (2\kappa_{FT})$  and  $\tau_{BL} = BLH^2 / (2\kappa_{BL})$ , where  $D$  is a free tropospheric depth parameter and  $BLH$  is boundary layer height. Pugh et al. (2012) suggest  $\kappa_{FT}$  should typically take values of between  $0.5 \text{ m}^2 \text{ s}^{-1}$  (under stable conditions) and  $1.5 \text{ m}^2 \text{ s}^{-1}$  (under more turbulent ones); Pisso et al. (2009) reported slightly lower values of  $0.3\text{--}1.0 \text{ m}^2 \text{ s}^{-1}$ . Typically,  $\kappa_{BL} = 10\kappa_{FT}$  whilst  $D$  takes values of roughly  $200\text{--}500 \text{ m}$ . We explore the impact of mixing subject to three different combinations of  $\kappa_{FT}$ ,  $\kappa_{BL}$  and  $D$  (Mix1, Mix2 and



coefficients in the two models (Squire et al., 2014, 2015), and we use 3-D fields of precipitation, output from UM-UKCA every 20 min timestep, to drive the wet deposition in CiTTyCAT. This is in addition to initialising the composition of air parcels in CiTTyCAT with the concentrations of species simulated in UM-UKCA (subject to the same chemical mechanism) as described at the end of the last section.

### 2.3 CheT and CheT2 chemical mechanisms

The standard tropospheric chemistry mechanism, CheT, includes 56 chemical tracers and 165 photochemical reactions, of which 16 tracers and 44 reactions comprise the MIM (Pöschl et al., 2000). It is the result of a systematic reduction of version 2 of the Master Chemical Mechanism (MCM; Jenkin et al., 1997), in which species are lumped together based on their structure, for example all hydroxyperoxy radicals as “ISO<sub>2</sub>”. CheT2 differs only with respect to isoprene oxidation, with 24 tracers and 59 reactions in place of the previous 16 and 44 respectively, and is traceable to MCM version 3.2 (MCMv3.2). The differences, reflecting the updates compiled by Jenkin (2012) for the UK Met Office, are as follows:

1. Changes to the chemistry of first generation isoprene nitrates (ISON): NO<sub>x</sub> is regenerated from ISON in CheT by photolysis, or conversion to second generation nitrates (NALD), followed by reaction with OH; in CheT2, the yield of NO<sub>x</sub> from ISON is increased in line with the measurements of Perring et al. (2009) by increasing the rate of ISON photolysis and adding a further ISON + OH → NO<sub>2</sub> channel; CheT2 also includes the addition of O<sub>3</sub>-initiated ISON degradation (Lockwood et al., 2010).
2. The inclusion, as mentioned in Sect. 1, of a route by which OH initially consumed in isoprene oxidation may be efficiently regenerated at low ambient NO<sub>x</sub> concentrations: the formation of hydroperoxy-aldehydes (HPALDS) from hydroperoxy radicals (ISO<sub>2</sub>) and their subsequent rapid release of OH (Peeters et al., 2009; Crouse et al., 2011).

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3. The inclusion of the formation of isoprene epoxydiols (IEPOX) from the oxidation of isoprene hydroxyl-hydroperoxides (ISOOH); Paulot et al. (2009) identified these as a potential source of secondary organic aerosols.

4. A reduction in the yield of peroxyacetylic nitric anhydride (MPAN) from isoprene oxidation relative to that adopted in CheT; see Jenkin (2012) for details.

In this study, however, we are less concerned with the differences between the two mechanisms, which have already been explored at length (see, e.g., Archibald et al., 2010a, b; Squire et al., 2015), than we are with their relative abilities to reproduce observations of atmospheric composition above the Amazon rainforest – and the latter subject to different model frameworks (Eulerian and Lagrangian) and trace-gas emissions.

### 2.4 Trace gas emissions

The trace gas emissions are comprised of: anthropogenic emissions taken from EDGAR version 4.2 (<http://edgar.jrc.ec.europa.eu>); and biogenic emissions calculated with the Organising Carbon and Hydrology In Dynamic Ecosystems land surface model (ORCHIDEE), with the exception of NO<sub>2</sub> emissions from soils that are taken from the Global Emissions Inventory Activity (GEIA; Yienger and Levy, 1995). The annual total emission of each species, globally, is given in Table 3, including its breakdown into anthropogenic and biogenic components.

We employ EDGAR 4.2 emissions of NO<sub>2</sub>, CO and NMVOCs from all sectors apart from “Non-road transportation” (1A3a + c + d + e in the nomenclature of the Intergovernmental Panel on Climate Change; IPCC), since the latter includes aircraft emissions that are difficult to implement in the Lagrangian model; CH<sub>4</sub> is treated as a constant field (1.76 ppmv). We adopt the most recent emissions available, which correspond to the year 2008. Available at a spatial resolution of up to 0.1° × 0.1° globally, these are capable of resolving a city of approximately 10 km × 10 km in the tropics, such as Manaus. We note, however, that they do not include any seasonality; we expect the

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seasonality to be relatively low in the tropics. The NMVOC emissions come lumped together as a single carbon flux. We derive emissions of ethane ( $C_2H_6$ ), propane ( $C_3H_8$ ), formaldehyde (HCHO), acetone ( $CH_3C(O)CH_3$ ) and acetaldehyde ( $CH_3CHO$ ) from this using the IPCC (2002)'s speciation of industrial- and biomass burning emissions; see their Table 4.7(b). This speciation is crude: we assume, for example, that “ketones” are entirely comprised of  $CH_3C(O)CH_3$ , and “other aldehydes” solely  $CH_3CHO$ . However, our priority is to start from anthropogenic emissions of sufficient spatial resolution to resolve the city of Manaus, and EDGAR 4.2 is unique in providing emissions of this resolution, globally. The CiTTYCAT integrations employing “High res” emissions exploit their full  $0.1^\circ \times 0.1^\circ$  resolution. For use in UM-UKCA, and the CiTTYCAT integrations employing “UKCA res” emissions, the emissions are degraded to  $3.75^\circ \times 2.5^\circ$ ; see Table 2 and accompanying text.

As stated above, biogenic emissions of  $C_5H_8$ , HCHO,  $CH_3C(O)CH_3$  and  $CH_3CHO$  are calculated with ORCHIDEE. This includes parameterisations based on Guenther et al. (1995) and Lathièrè et al. (2006), modified according to Guenther et al. (2012) and more recent findings to take into account the progress of our knowledge in this field (see Messina et al., 2015). ORCHIDEE is forced with 2012 National Centers for Environmental Prediction meteorological analyses (NCEP v5.3) from the Climatic Research Unit of the US National Centre for Atmospheric Research. These daily (24 h average) emissions are used at full spatial resolution ( $0.5^\circ \times 0.5^\circ$ ) in the “High res” integrations with CiTTYCAT but, just as for the anthropogenic emissions, degraded to  $3.75^\circ \times 2.5^\circ$  for use in UM-UKCA and the CiTTYCAT integrations employing “UKCA res” emissions. We apply a diurnal cycle – the same in both models, based on the division of each 24 h period into 20 min intervals – to the emissions of  $C_5H_8$  but not HCHO,  $CH_3C(O)CH_3$  or  $CH_3CHO$ . The  $NO_2$  emissions from soils are taken from GEIA dataset, soilNOXmn1.1a (Yienger and Levy, 1995). In view of the uncertainty in these, they are used in both models, in all integrations, at a resolution of  $3.75^\circ \times 2.5^\circ$ .

Figure 2 illustrates the total “UKCA res” emissions of each species (anthropogenic + biogenic) on the 1 January and 1 July 2012. Recall, only the species including a bio-





higher  $[O_3]$  than UM-UKCA as it did at mid-to-high altitudes. But, continuing to examine flight B735, what is interesting is that the  $[O_3]$  simulated in CiTTYCAT at low altitudes differs markedly from that with which it is initialised, consistent with this being strongly influenced by intervening emissions, chemistry and/or dry deposition in the boundary layer en route. Recall that the corresponding air parcels spend much of the previous 7 days in the boundary layer; see Sect. 2.1.1. The decrease in  $[O_3]$  from around 50 ppbv upon initialisation to about 15 ppbv on the flight track suggests that the dry deposition of  $O_3$  to the forest, the direct reaction of  $O_3$  with  $C_5H_8$  (at low ambient  $[NO_x]$ ), or a combination of the two, is highly influential.

Comparing modelled and measured  $[NO]$ , the top panel of Fig. 5 does not present a simple picture. CiTTYCAT shows reasonably good agreement at low altitudes but a tendency, at least in places, to overestimate measured  $[NO]$  at mid-to-high altitudes, perhaps contributing to its overestimation of  $[O_3]$  here. Meanwhile, UM-UKCA shows generally good agreement at higher altitudes but a tendency to overestimate  $[NO]$  in and near the boundary layer, possibly contributing to its overestimation of  $[O_3]$  in these portions of the flight. The agreement between each model and the measurements for  $[NO_2]$ , though imperfect, is reasonably good; see bottom panel of Fig. 5. We note that CiTTYCAT simulates higher  $[NO_2]$  than UM-UKCA shortly after 13:00 UT and, in doing so, overestimates the measurements. CiTTYCAT's underestimation of  $[O_3]$  in this portion of the flight (see earlier) does not therefore appear to be due to a lack of  $[NO_x]$ . We speculate, instead, that this could be due to a lack of vertical mixing – a lack of ventilation of the boundary layer and hence exchange with free tropospheric air of higher  $[O_3]$ . Likewise, CiTTYCAT's overestimation of  $[O_3]$  in mid-to-high altitude portions of the flight could reflect a lack of vertical mixing within the free troposphere, and thus the relaxation of elevated values of  $[O_3]$  (with which the air parcels are initialised; 50–90 ppbv) towards lower background concentrations. Subject to the same emissions (UKCA res), CiTTYCAT consistently simulates considerably higher  $[O_3]$  than UM-UKCA at mid-to-high altitudes: this is observed across all five flights (see Figs. S1–S4).

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chemical mechanism and an increase in the resolution of trace gas emissions. The switch from CheT to CheT2 chemistry, for example, may be expected to reduce the  $[C_5H_8]$  simulated in both models on account of including an OH “recycling” mechanism (see Sect. 2.3).

Finally, we compare modelled and measured  $[CO]$  in Fig. 7. Note that the high/low  $[CO]$  values at approximately one hour intervals correspond to the “span/zero” in-flight calibrations of the VUV fluorescence CO monitor (see Sect. 2.1.4). UM-UKCA generally underestimates the measurements, simulating around 100 ppbv throughout the flight; this is understood to be linked to a general high bias in  $[OH]$ , and hence a low bias in CO lifetime, in this version of the model (see, e.g., Telford et al., 2013). Meanwhile, CiTTYCAT simulates near identical concentrations to UM-UKCA in the mid-to-high altitude portions of the flight, but considerably higher  $[CO]$  at low altitudes. These higher concentrations overestimate the measurements – possibly the result of overestimating  $[C_5H_8]$ , and hence overestimating the production of CO from  $C_5H_8$  oxidation. A lack of boundary-layer ventilation in CiTTYCAT, and hence a lack of exchange between air with high  $[CO]$  in the boundary layer and free tropospheric air of lower  $[CO]$ , could again contribute. The low bias in  $[CO]$  simulated with UM-UKCA extends across all five flights (see Figs. S1–S4); the difference in behaviour between the two models clearly extends to flights B749 and B750 (Figs. S3 and S4) but is less pronounced on flights B744 and B745 (Figs. S1 and S2).

### 3.2 Comparing chemical mechanisms (CheT and CheT2)

We find that the chemical mechanism employed has a negligible effect on the  $[O_3]$ , and only a modest effect on the  $[NO]$ ,  $[NO_2]$ ,  $[C_5H_8]$  and  $[CO]$ , we simulate for flight B735 in UM-UKCA and CiTTYCAT (see Fig. 8). The impact of switching from CheT to CheT2 for  $[NO]$  and  $[NO_2]$  is largely limited to the low altitude portions of the flight in which  $C_5H_8$  is encountered. This is consistent with the direct changes to the chemistry being limited to ones relating to ISON (the lumped species comprised of first generation isoprene nitrates); see Sect. 2.3. To first order, we would expect the increase in the

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relaxation, Mix1, yields the best agreement between modelled and measured  $[C_5H_8]$ . Indeed, the agreement is excellent. However, Mix1 yields the worst agreement between modelled and measured  $[O_3]$  in the low altitude portions of the flight – in these regions, considerably worse than the simulation without mixing, consistently overestimating the measurements by 15–20 ppbv in absolute terms, and close to 100 % in relative terms. The slower relaxations, Mix 2 and Mix 3, yield somewhat higher  $[C_5H_8]$  – greater than that measured but a significant improvement over that simulated with CiTTyCAT without mixing, and better in two out of three portions of the flight than that simulated with UM-UKCA. Mix2 and Mix3, meanwhile, yield better agreement between modelled and measured  $[O_3]$  in the low altitude parts of the flight. Furthermore, Mix3 starts to retain some of the structure in  $[O_3]$  simulated in the high altitude portions of the flight that is almost entirely absent from the simulation with UM-UKCA but present, at least to some extent, in the measurements; see earlier discussion in Sect. 3.1. Judging by the structure present in the  $[O_3]$  measured in these parts of the flight, there could be justification for still slower relaxation in the free troposphere. The mixing formulation could be iterated further, however, of the three formulations applied here (exploring the range of parameter values suggested in the literature; see Sect. 2.2.2 and Table 1), we judge Mix3 to be the most appropriate overall.

### 3.5 Modelling atmospheric chemistry downwind of Manaus

We now move from what has predominantly been an exploration in the spatial domain – in other words, comparing modelled and measured trace gas concentrations on flight tracks – to an exploration of the temporal domain. We simulate  $[O_3]$  at a single site downwind of Manaus over an extended period of time, the month in which all five case-study SAMBBA flights took place. Recall, back-trajectories were calculated from a boundary layer site (61.0° W, 3.1° S, 900 hPa) roughly 100 km downwind (1° west) of Manaus at 6 hourly intervals throughout September 2012. The choice of site is arbitrary; we are not aware of any measurements of  $[O_3]$  at this site or comparable sites, during the period in question, with which to compare the  $[O_3]$  we simulate –

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imum, absolute maximum, median, and 25th and 75th percentile values of simulated  $[O_3]$  are included in the top right.

In the absence of vertical mixing, the  $[O_3]$  simulated with CiTTYCAT (dotted green line) exhibits much more structure than that simulated with UM-UKCA (dashed blue line), frequently exceeding 50 ppbv and exceeding 75 ppbv on seven occasions. Depending on the speed of relaxation imposed, this structure is suppressed to a greater or lesser extent, and the simulations with CiTTYCAT (solid red, blue and green lines) can generate more or less variability in the time series than UM-UKCA. Mixing formulation, Mix3, judged in the last section to yield best agreement between modelled and measured  $[O_3]$  over a range of altitudes, including specifically low altitudes, yields a distribution of  $[O_3]$  that has a higher median value than UM-UKCA (34.0 cf. 31.7 ppbv), a higher 75th percentile (38.3 cf. 34.9 ppbv), and a higher absolute maximum (54.3 cf. 41.7 ppbv). The  $[O_3]$  simulated with UM-UKCA never exceeds 50 ppbv in this period, whilst that simulated with CiTTYCAT, subject to Mix3, does so five times. This shift towards higher  $[O_3]$  leads to an 8 % increase in mean  $[O_3]$  simulated throughout the month, from 32.5 to 35.1 ppbv. Note that the “AOT40” we calculate over just 30 days increases by a factor of almost 40, from 22.6 to 863 ppbv h.

In the bottom left of Fig. 11, we explore the effects on the simulation of  $[O_3]$  with CiTTYCAT, subject to Mix3, of changing from CheT to CheT2 chemistry and/or degrading the resolution of the emissions to that used in UM-UKCA ( $3.75^\circ \times 2.5^\circ$ ); the corresponding box and whisker plots are included in the bottom right. Only modest differences arise. The switch to CheT2 chemistry yields substantially different  $[O_3]$  only on two days (21 and 24 September); compare the green and red lines. Meanwhile, degrading the resolution of the emissions has little effect throughout; compare the solid and dotted lines. Our earlier findings appear to hold irrespective of the chemistry and emissions employed: CiTTYCAT (Mix3) yields much more structure in  $[O_3]$  than UM-UKCA, exceeding 50 ppbv on four or five occasions as opposed to none; and, whilst the mean  $[O_3]$  increases by approximately 10 %, or 3 ppbv, “AOT40” increases by a factor of roughly 40–60; see Table 4. Whilst our study was not designed to calculate flux-based

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included neither explicit vertical mixing in the boundary layer (due to convection) nor ventilation of the boundary layer and exchange with air in the free troposphere. It is to the latter that we attribute the Lagrangian model's overestimation of  $[C_5H_8]$  in the boundary layer and  $[O_3]$  in the free troposphere; we believe they are the result of a lack of mixing with, and hence dilution by, lower  $[C_5H_8]$  air above and lower  $[O_3]$  air below respectively (see Sect. 3.1 and, earlier, Sect. 2.2.2).

The simple approach to diffusive vertical mixing that we later introduced into the Lagrangian model has been used in previous studies; see Pugh et al. (2012) and the references contained therein. It comprised: the relaxation of species of "intermediate lifetimes" towards 3-D monthly mean concentrations simulated in the Eulerian model; and the relaxation of short-lived species (all other species besides  $CH_4$ ) towards zero concentrations (characteristic of the free troposphere). Recall that  $[CH_4]$  was fixed in the model. The relaxation was applied on timescales  $\tau_{BL}$  and  $\tau_{FT}$  in the boundary layer and free troposphere respectively; see Sect. 2.2.2 and Table 1 for more details. Having explored just three combinations of  $\tau_{BL}$  and  $\tau_{FT}$  spanning literature values, we cannot claim to have fully optimised this simple treatment of mixing. Predictably, however, all three formulations brought the Lagrangian simulations more closely in line with their Eulerian counterparts; see Sect. 3.5. Moreover, one formulation, Mix3 ( $\tau_{BL} = 27.8$  h, subject to a boundary layer height of 1000 m, and  $\tau_{FT} = 69.4$  h) yielded the desirable combination of: reasonable agreement with measurements of both  $[O_3]$  and  $[C_5H_8]$  at low altitudes; and structure in the simulated  $[O_3]$  reminiscent of that exhibited by the measurements. It was predominantly this formulation that we subsequently applied to a simulation of boundary layer  $[O_3]$ .

We should note at this point that the  $[O_3]$  simulated by this combination of Lagrangian and Eulerian models (subject to Mix3) did not show as good agreement with the measurements at low altitudes as that simulated with the Lagrangian model alone: the Lagrangian model simulated 10–15 ppbv lower  $[O_3]$  than the combination of models (and the Eulerian model on its own), in closer agreement with the measurements. It may have done so, however, for the wrong reason. If the lack of vertical mixing in the

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for Atmospheric Science, University of Cambridge, for their generous welcome whilst working remotely there as a visiting researcher.

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**Table 1.** Parameters subject to which mixing is explored in formulations, Mix1–3:  $\kappa_{\text{FT}}$  and  $\kappa_{\text{BL}}$  are free-troposphere and boundary-layer diffusion coefficients;  $D$  is a free tropospheric depth parameter.  $\tau_{\text{FT}}$  and  $\tau_{\text{BL}}$  are the resulting free-troposphere and boundary-layer relaxation timescales, the latter when subject to a boundary layer height (BL height) of 1000 m.

Formulation	$\kappa_{\text{FT}}$ ( $\text{m}^2 \text{s}^{-1}$ )	$\kappa_{\text{BL}}$ ( $\text{m}^2 \text{s}^{-1}$ )	$D$ (m)	$\tau_{\text{FT}}$ (h)	$\tau_{\text{BL}}$ (h)
Mix1	1.5	15.0	200	3.7	9.3
Mix2	0.5	5.0	200	11.1	27.8
Mix3	0.5	5.0	500	69.4	27.8

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**Table 2.** Main features of the eight CiTTYCAT model setups, including: the UM-UKCA integration used to initialise the composition of air parcels; the chemical mechanism employed; the trace gas emissions used; and the inclusion, or otherwise, of mixing subject to formulations Mix1–3.

CiTtYCAT model setup	Initialisation	Chemistry	Emissions	Mixing
1. CiTtYCAT (CheT)	UM-UKCA (CheT)	CheT	UKCA res	None
2. CiTtYCAT (CheT2)	UM-UKCA (CheT2)	CheT2	UKCA res	None
3. CiTtYCAT (CheT, HRE)	UM-UKCA (CheT)	CheT	High res	None
4. CiTtYCAT (CheT2, HRE)	UM-UKCA (CheT2)	CheT2	High res	None
5. CiTtYCAT (CheT, Mix1–3)	UM-UKCA (CheT)	CheT	UKCA res	Mix1–3
6. CiTtYCAT (CheT2, Mix1–3)	UM-UKCA (CheT2)	CheT2	UKCA res	Mix1–3
7. CiTtYCAT (CheT, HRE, Mix1–3)	UM-UKCA (CheT)	CheT	High res	Mix1–3
8. CiTtYCAT (CheT2, HRE, Mix1–3)	UM-UKCA (CheT2)	CheT2	High res	Mix1–3

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**Table 3.** Global trace gas emission totals (employed in all integrations), including the total anthropogenic and biogenic contributions.

Tg (species) yr <sup>-1</sup>	NO <sub>2</sub>	CO	HCHO	C <sub>2</sub> H <sub>6</sub>	C <sub>3</sub> H <sub>8</sub>	CH <sub>3</sub> C(O)CH <sub>3</sub>	CH <sub>3</sub> CHO	C <sub>5</sub> H <sub>8</sub>
Anthropogenic	99.0	875	2.37	9.85	9.46	4.35	6.54	0.0
Biogenic	17.8	0.0	4.21	0.0	0.0	39.4	14.3	401
Total	117	875	6.57	9.85	9.46	43.7	20.8	401

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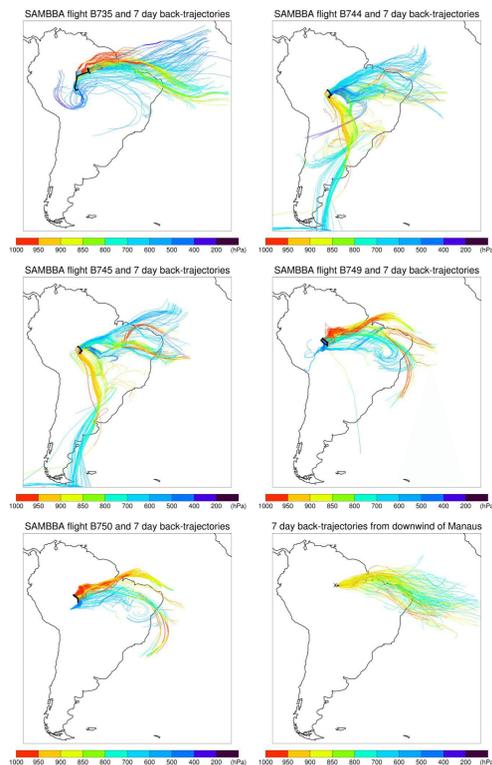
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**Table 4.** Metrics regarding the  $[O_3]$  simulated downwind of Manaus in UM-UKCA and CiTTyCAT, subject to CheT and CheT2 chemical mechanisms; all integrations with CiTTyCAT employ mixing formulation Mix3, and those labelled “HRE” employ High res emissions. See text for a discussion of the accumulation time for the reported AOT40-like metric, labelled “AOT40”.

Simulated $[O_3]$ metric	UM-UKCA		CiTTyCAT (Mix3)			
	CheT	CheT2	CheT, HRE	CheT2, HRE	CheT	CheT2
No. of times $[O_3] > 50$ ppbv	0	0	5	5	4	5
Mean $[O_3]$ (ppbv)	32.5	32.5	35.1	35.9	35.0	36.0
Increase in mean $[O_3]$ relative to UM-UKCA (subject to same chemistry)	–	–	2.6 ppbv +8 %	3.4 ppbv +11 %	2.5 ppbv +8 %	3.5 ppbv +11 %
“AOT40” (ppbv h)	22.6	17.5	863	1081	889	1091
Increase in “AOT40” relative to UM-UKCA (subject to same chemistry)	–	–	841 ppbv h 38×	1063 ppbv h 62×	866 ppbv h 39×	1073 ppbv h 62×



**Figure 1.** Flight tracks (black lines), and 7 day back-trajectories arriving on these at one minute intervals (coloured according to pressure), for SAMBBA flights B735, B744, B745, B749 and B750; see text for details. Bottom right: 7 day back-trajectories arriving at a site roughly 100 km downwind ( $1^\circ$  west) of Manaus at 6 hourly intervals throughout September 2012 (coloured according to pressure); “x” marks the site ( $61.0^\circ$  W,  $3.1^\circ$  S) and the black dot marks Manaus.

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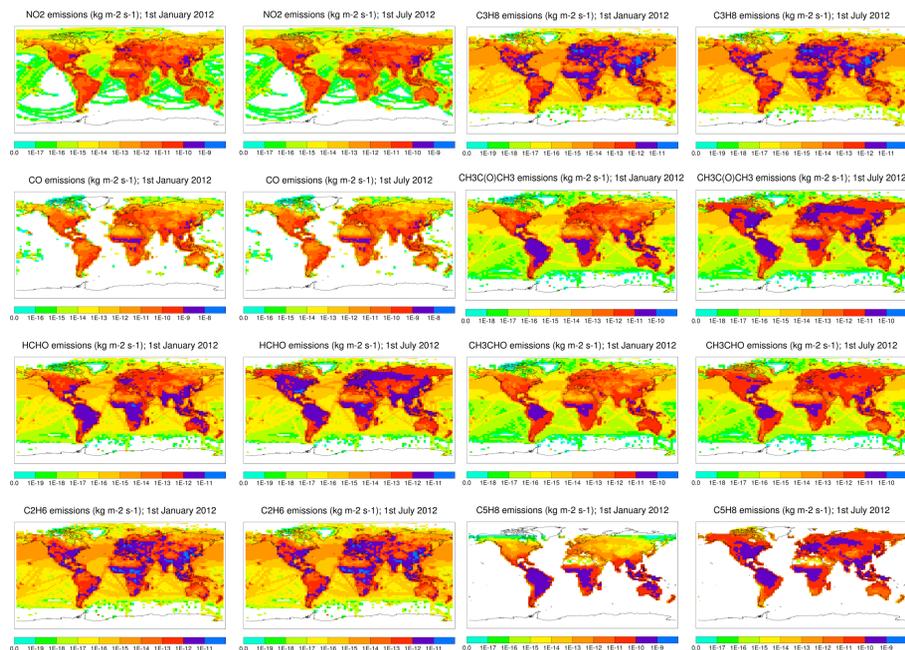
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**Figure 2.** Total (anthropogenic + biogenic) trace gas emissions at 3.75° longitude × 2.5° latitude on 1 January and 1 July 2012, employed in UM-UKCA (run in “climate mode”) and “UKCA res” integrations with CiTTyCAT.

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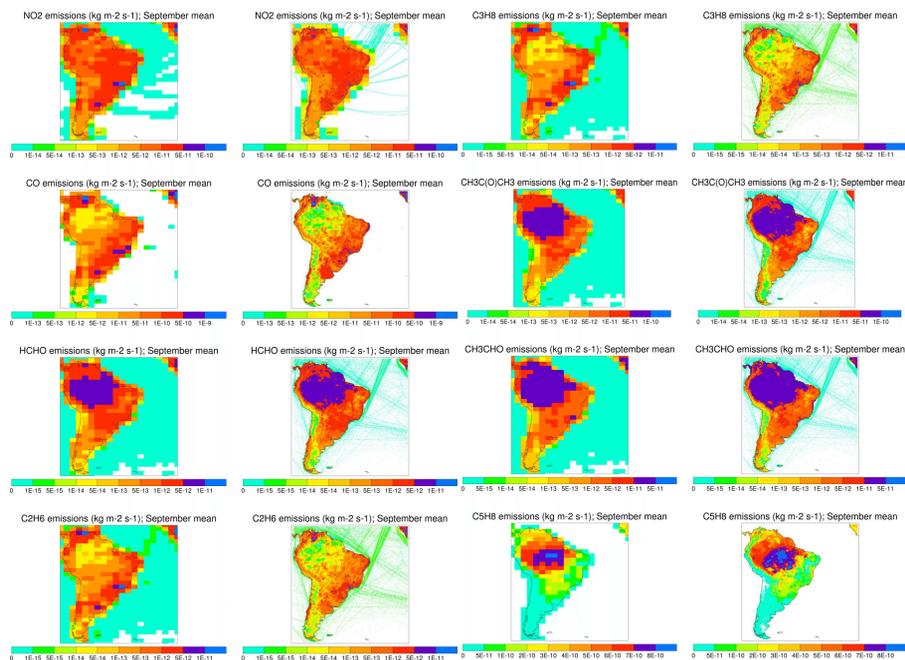
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**Figure 3.** Total (anthropogenic + biogenic) trace gas emissions employed in CiTTyCAT “UKCA res” integrations (left) and “High res” integrations (right); all emissions are September 2012 monthly means, focussing on South America.

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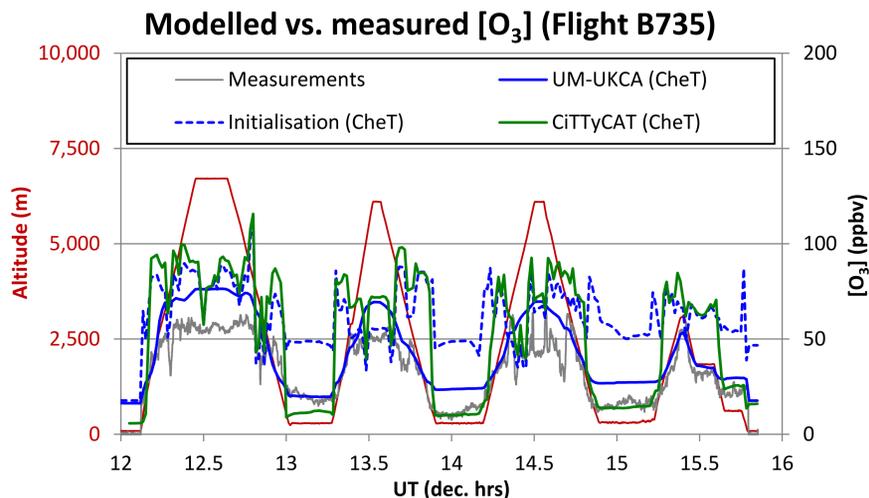
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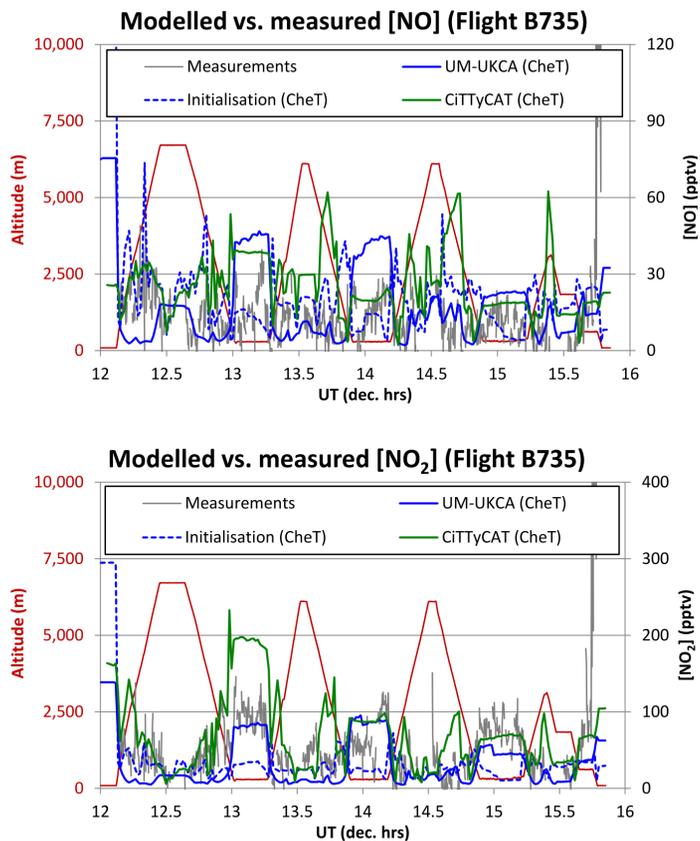


**Figure 4.**  $[O_3]$  measured on SAMBBA flight B735 and simulated in UM-UKCA (CheT) and CiTTYCAT (CheT). The  $[O_3]$  with which CiTTYCAT is initialised is also illustrated; see text for details.

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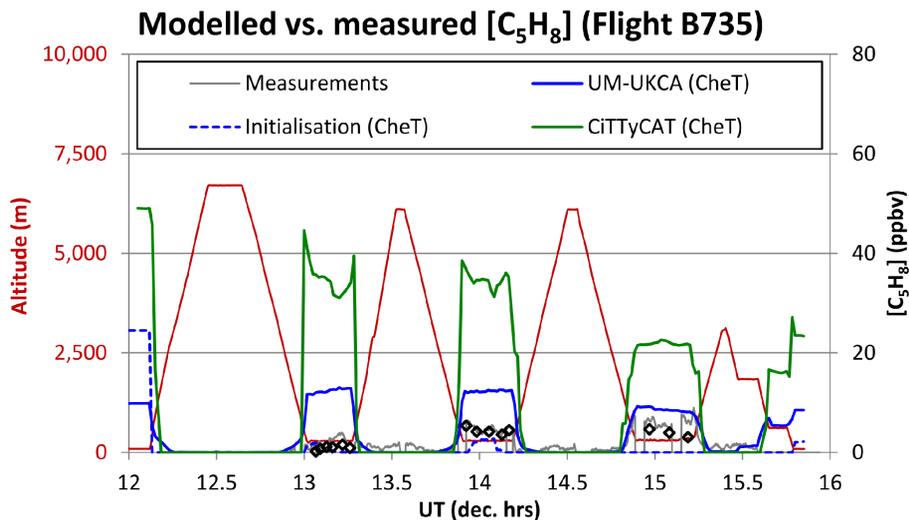


**Figure 5.** [NO] and [NO<sub>2</sub>] measured on SAMBBA flight B735 and simulated in UM-UKCA (CheT) and CiTTYCAT (CheT). The [NO] and [NO<sub>2</sub>] with which CiTTYCAT is initialised are also illustrated; see text for details.

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**Figure 6.**  $[C_5H_8]$  measured on SAMBBA flight B735 and simulated in UM-UKCA (CheT) and CiTTYCAT (CheT). The  $[C_5H_8]$  with which CiTTYCAT is initialised is also illustrated; the open black diamonds correspond to the  $[C_5H_8]$  measurements based on whole air samples.

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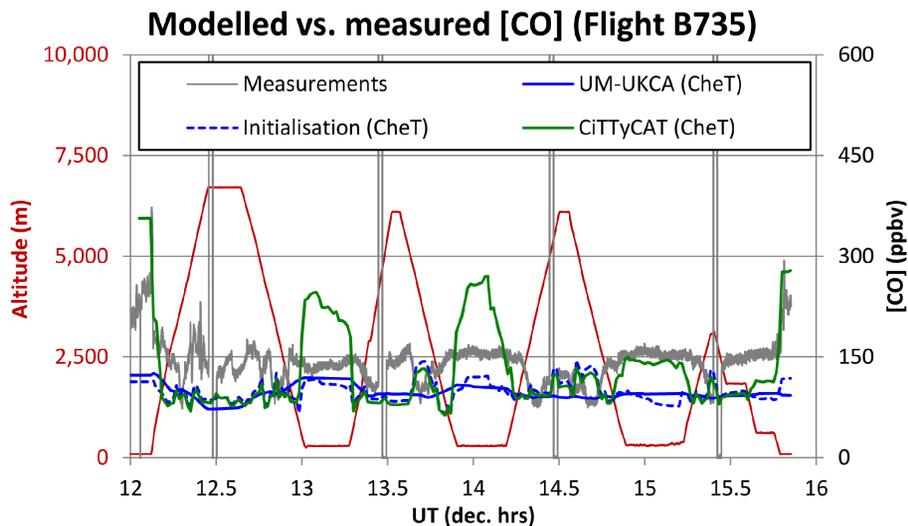
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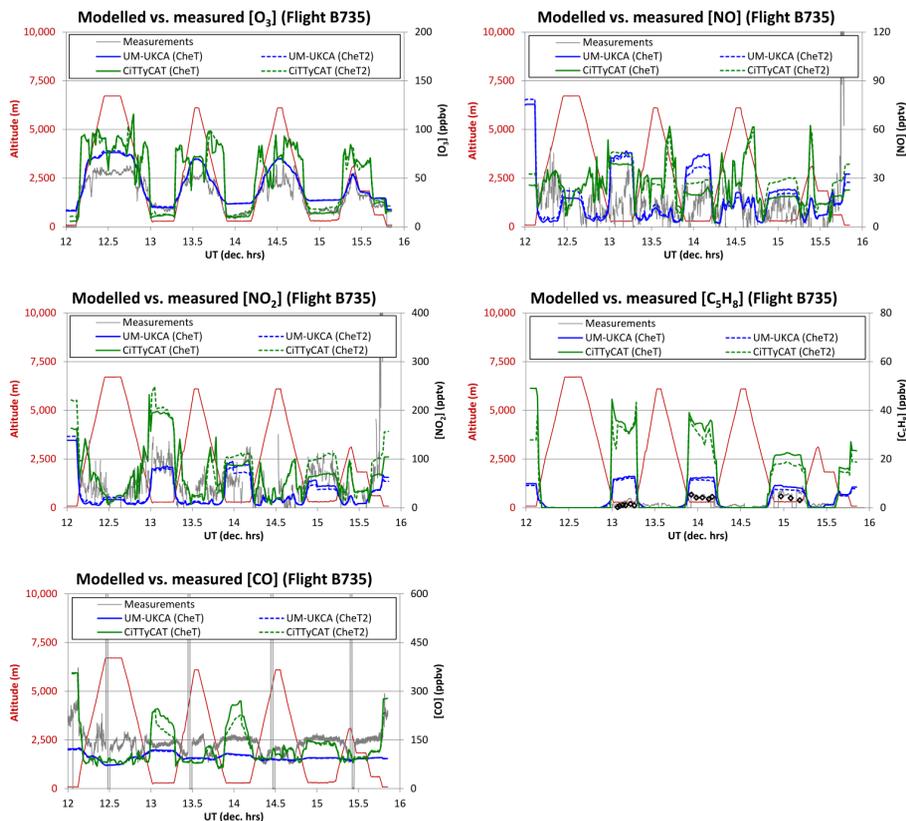
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**Figure 7.** [CO] measured on SAMBBA flight B735 and simulated in UM-UKCA (CheT) and CiTTYCAT (CheT). The [CO] with which CiTTYCAT is initialised is also illustrated; see text for details.

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**Figure 8.**  $[O_3]$ ,  $[NO]$ ,  $[NO_2]$ ,  $[C_5H_8]$  and  $[CO]$  measured on SAMBBA flight B735 and simulated in UM-UKCA and CiTTYCAT, subject to CheT and CheT2 chemical mechanisms (see Sect. 2.3 for more details); the open black diamonds correspond to  $[C_5H_8]$  measurements based on whole air samples.

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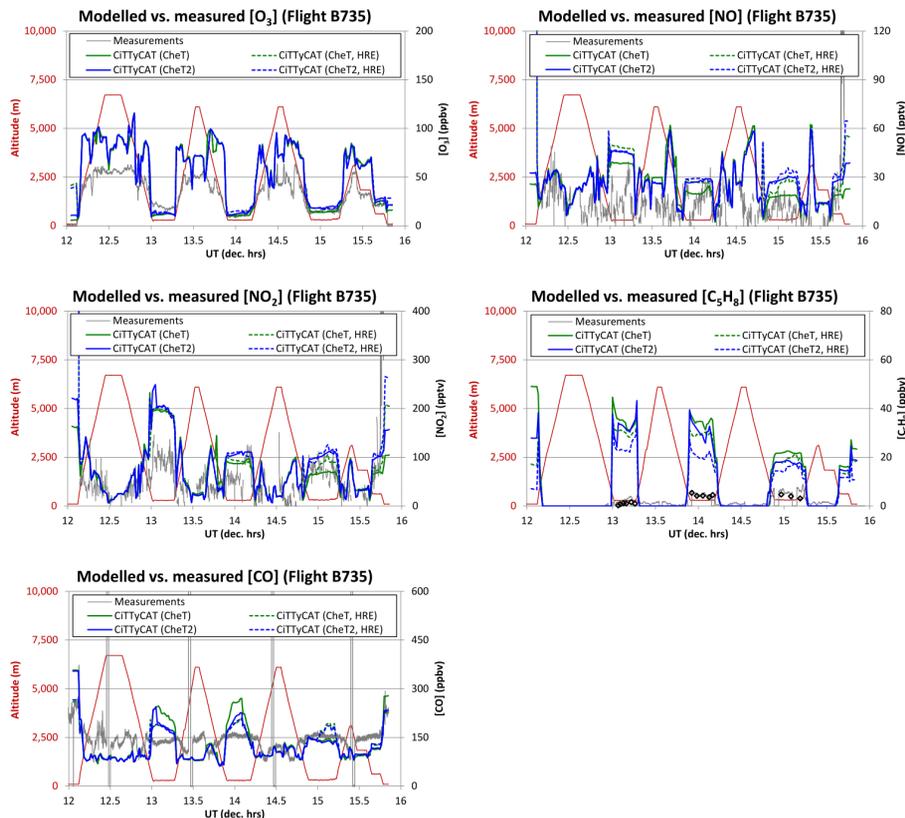
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**Figure 9.**  $[O_3]$ ,  $[NO]$ ,  $[NO_2]$ ,  $[C_5H_8]$  and  $[CO]$  measured on SAMBBA flight B735 and simulated in CiTTYCAT, subject to CheT and CheT2 chemical mechanisms (see Sect. 2.3) and both “UKCA res” emissions and “High res” emissions (HRE; see Sect. 2.4 for more details); the open black diamonds correspond to  $[C_5H_8]$  measurements based on whole air samples.

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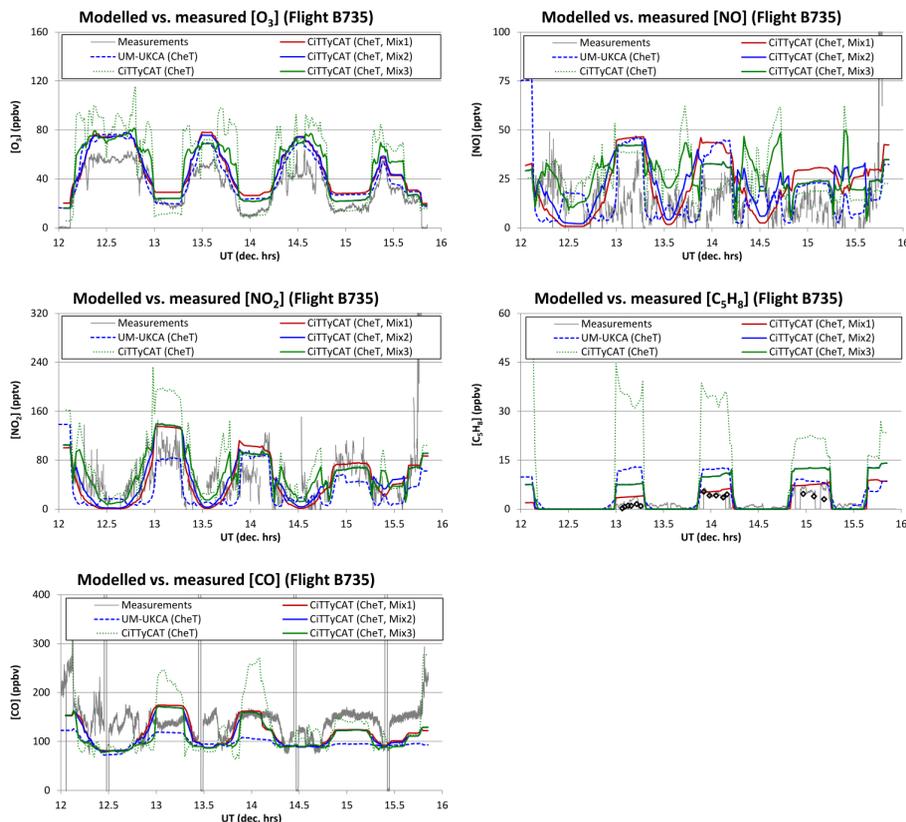
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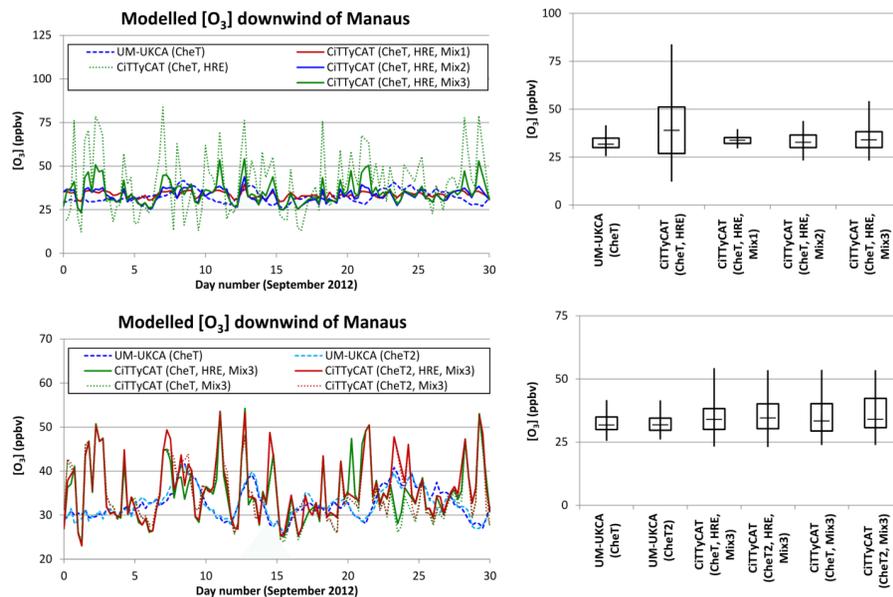
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**Figure 10.**  $[O_3]$ ,  $[NO]$ ,  $[NO_2]$ ,  $[C_5H_8]$  and  $[CO]$  measured on SAMBBA flight B735 and simulated in UM-UKCA (CheT) and CiTTyCAT (CheT), the latter subject to no mixing and, subsequently, three formulations of simple diffusive vertical mixing (relaxation towards background values) as outlined in Sect. 2.2.2 and Table 1; the open black diamonds correspond to  $[C_5H_8]$  measurements based on whole air samples.

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**Figure 11.** Left: [O<sub>3</sub>] simulated approximately 100 km downwind of Manaus in UM-UKCA and CiTTYCAT; the top panel compares CiTTYCAT integrations, all employing the CheT chemical mechanism but differing with respect to mixing formulation (Mix1–3; see Sect. 2.2.2 and Table 1 for more details), whilst the bottom panel compares CiTTYCAT integrations, all employing mixing formulation, Mix3, but differing with respect to the chemical mechanism (CheT or CheT2) and/or the resolution of trace gas emissions employed (HRE = High res ems). Right: the corresponding “box and whisker” plots of the minimum, maximum, median, and first- and third quartile [O<sub>3</sub>] values. The UM-UKCA (CheT) and CiTTYCAT (CheT, HRE, Mix3) runs are included in both top and bottom panels.

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