

Interactive comment on “Observed and simulated global distribution and budget of atmospheric C₂–C₅ alkanes” by A. Pozzer et al.

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We thank the anonymous referee #2 for the constructive comments.

Reply to major comments:

1. We agree with the referee that a more quantitative approach is useful for supporting our conclusions.

Therefore, we calculated the main statistical quantities and resume them in Taylor diagrams (Taylor, 2001) for a complete overview without increasing drastically the

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length of the manuscript. The diagrams (one for each C_4 – C_5 species) show at a glance the location (latitude) of the stations (color code) and the different simulations (symbol). Moreover, we decided to weight the correlations and biases between the simulations and observations by the geometric mean of model variability (standard deviation from the averaged output values) and measurement variability (monthly standard deviation of the measurements from their average). For further details of this approach, we refer to Jöckel et al. (2006, appendix D). This weighting preserves the relationship between the three statistical quantities visualised in the Taylor diagram. However, locations with a high variability, i.e., where absolute differences are less significant since single measurements are less representative, have less weight. Values which are more representative for the average conditions are weighted stronger, thus suppressing specific episodes that cannot be expected to be reproduced by the model. The results of these calculations are shown in the figures of this reply, (Figs. 1-4) where the results from simulation *E1* and simulation *E2* are depicted with circles and squares, respectively. The color denotes the latitude (as in the color bar). By the help of this additional analysis we find that there is overall a much better agreement between the model simulations and the observations in the Northern Hemisphere (NH) extratropics than in the Southern Hemisphere (SH) extratropics, and that the deviation is largest in the tropics. More specifically:

- n-butane (Fig. 1): Results from simulation *E2* agree much better with the observations than results from simulation *E1*. Both simulations show a very high correlation with the observations (meaning that they correctly reproduce the seasonal cycle) for stations located between 40 °N and 90 °N. However, results from simulation *E2* are very close to the perfect correlation (empty square), whereas simulation *E1* generally overestimates the amplitude of the seasonal cycle (the standard deviation is larger than 1). For stations in the tropics, none of the two simulations agrees with the observa-

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tions: the amplitude of the seasonal cycle is systematically underestimated in both cases.

- i-butane (Fig. 2): In contrast to n-butane, the Taylor diagram for i-butane shows a less clear picture. Results from simulation *E1* and simulation *E2* are partially very similar. None of the simulations can be judged “better” and only at very high latitudes, simulation *E2* reproduces better the observations (with a lower centered pattern root mean square (RMS) difference). Again, in the SH none of the simulations yields satisfactory results.
- n-pentane (Fig. 3): Also for n-pentane the analysis does not clearly show which simulation is better in reproducing the observations. The comparison between simulation results and observations shows a very poor agreement at stations located in the tropics and in the SH. In the NH, at locations north of 60° N, the centered pattern RMS difference is similar for both simulations, whereas at locations between 20 and 30° N simulation *E1* is slightly better than simulation *E2*.
- i-pentane (Fig. 4): Although the results are not as clear as for n-butane, north of 60° N simulation *E2* yields lower centered pattern RMS differences than simulation *E1*. At these latitudes, the amplitude of the seasonal cycle is overestimated by at least 60% in simulation *E1* (visible from the normalised standard deviations), whereas it is within 40% in simulation *E2*. Nevertheless, results from simulation *E1* are closer to the observations compared to results from simulation *E2* for few stations with latitudes between 20 and 40° N. Again, a systematic underestimation of the observed mixing ratios is present for the SH stations, especially the one located in a remote region.

We will add the figures and the discussion in the revised manuscript.

2. We completely understand the point made by the referee, and we will discuss it. We agree that the emissions are not the only source of uncertainty in the

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model for the tracers, however, we firmly believe that emissions have the biggest contribution to it. Here (and in the revised manuscript), we briefly discuss the possible contributions to the uncertainties as suggested by the referee.

- Reaction kinetics: following the IUPAC (International Union of Pure and Applied Chemistry) recommendation for butanes and pentanes, the uncertainties in the reaction rates is of the order of 7%. In addition, the OH concentrations (the oxidant of these alkanes) are similar to the results obtained by Jöckel et al. (2006), which were shown to be consistent with numerous pre-cursor and reaction partner observations (see also below, reply to minor comments, 4)
- Chemical mechanism: The chemical mechanism does not increase the uncertainties of these tracers, but only those of theirs products. The main sink of the alkenes is the reaction with OH. We could hence argue that the products are misrepresented, but not the degradative reactions of alkanes. Nevertheless, a small uncertainty arises from the role of alternative sink reactions with Cl and NO₃, which contribute a few percent to the alkane degradation as described in the manuscript (see, as example, page 634 line 10).
- Meteorology: The model has been weakly nudged to the European Centre for Medium-Range Weather Forecasts (ECMWF) analysis (Jeuken et al., 1996; Jöckel et al., 2006, and references therein). This implies that the general circulation model is following the meteorology (at synoptic scale) as assimilated by the ECMWF analysis, which takes advantage of more than 75 million observations in a 12 hours period (98% of them are from satellites). We refer to the ECMWF (<http://www.ecmwf.int>) for further information. The uncertainties connected with the weak nudging (or better, due to the internal variability of the model which remains despite the nudging) can be estimated by the differences of meteorological parameters between

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the two simulations. This has been already discussed in a previous study (Pozzer et al., 2009), where differences of $\sim 15\%$ have been found between two different simulations for temperature and relative humidity. It must be stressed, however, that the usage of monthly averages in our calculation drastically decreases the uncertainties arising from the differences in the meteorology (due to the models internal variability), which remain despite the weak nudging. As we estimated earlier (Pozzer et al., 2009), the differences in the temperature and relative humidity are well below 5% once monthly averages are considered. We hence expect to reproduce consistently the meteorology calculated by the ECMWF analysis. Nevertheless, for the overall representation of the real meteorology, we rely on the ECMWF data assimilation, which has been evaluated previously (see for example Bozzano et al. (2004) or Salstein et al. (2008) for comparisons with surface observations). An even more detailed discussion about the quality of the ECMWF data product is far beyond the scope of our manuscript. Following Bozzano et al. (2004), for temperature, pressure and humidity, a very low relative difference between ECMWF analysis data and measurements is observed, while for the wind speed a relative difference of up to 100% of the simulated value are estimated from the observations. These uncertainties do not translate directly into uncertainties in the simulated alkanes mixing ratios, due to the non-linearity of the system. In addition, errors in estimating different meteorological parameters have different direct/indirect effects on the chemistry of alkanes. Nevertheless, Bozzano et al. (2004) also showed that when long time averages are considered (as in our case), the difference between observations and simulated parameters are by far lower. Therefore we estimate an upper uncertainty limit of the simulated alkanes of $\sim 100\%$ of the simulated value.

- Model resolution: We agree that the model resolution might be a crucial point that should be taken in account. In our manuscript we suggested to in-

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crease the resolution for further studies in order to address some questions that remain unanswered (see conclusions, line 28, page 633). Uncertainties arising from the resolution are twofold:

- uncertainties related to the meteorology. These uncertainties are included in the "meteorology", discussed above. In our applications the EMAC model has been weakly nudged towards the ECWMF analysis, i.e., guiding the simulated meteorology along the assimilated meteorology on the synoptical scale. Although it is expected that an increased resolution improves the representation of the meteorological parameters on scales smaller than the synoptic scale (in space and time), on the synoptic scale, however, the same pattern of the ECMWF analysis are followed and reproduces consistently.
- uncertainties related to chemical processes (mainly due to mixing/dilution of tracers). As example, high mixing ratios due to local emissions, present in the measurements, cannot be reproduced in the model due to the too large grid cells. We also partially mentioned this problem in the manuscript page 627, line 12. In our study, however, we used the observation from flask samples, analyzed by the *NOAA ESRL GMD*. As pointed out by Haas-Laursen and Hartley (1997), these flask samples have been collected under non-polluted conditions, i.e., for stations close to local sources only certain wind directions have been selected to avoid local contamination. Moreover, most of the stations are in remote regions, where background conditions are sampled. We can hence conclude that an increased resolution could help only at a few stations (i.e., in industrialized areas or where the sporadic biomass burning emissions are important), while for the majority of them, the resolution used in this study is sufficient to reproduce the chemical history of the $C_2 - C_5$ alkanes.
- Emissions : The differences resulting from the two emissions sets in simu-

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lation $E1$ and simulation $E2$ for butanes and pentanes can be up to a factor of 4 in a single grid box, depending on the location. We expect that the mixing ratios of butanes and pentanes are linearly dependent on the emissions, due to the negligible differences in the OH concentrations between the two simulations $E1$ and $E2$ (see reply to minor comments). We hence estimate the simulated mixing ratio uncertainties due to different emissions to be up to $\sim 300\%$ of the simulated tracer mixing ratio, depending on the location.

Following this analysis, we completely agree that emissions are not the only source of uncertainties in the simulated alkanes mixing ratios. Nevertheless, they contribute as the *main* source of uncertainty, and a correct estimate of the emissions could drastically reduce the uncertainties/error in the simulated alkanes mixing ratios.

3. We will modify the abstract following the referees suggestions.

Reply to minor comments:

1. As suggested by the referee, we will include a table resuming the different emissions used in the various simulations. This will indeed improve the readability.
2. We agree with the referee that the text can be improved merging many paragraphs. We will modify the text, in particular section 2 and section 5.
3. We correct this.
4. We thank the anonymous referee for pointing out the missing references. The KPP (Kinetic PreProcessor) software (Sandu and Sander, 2006; Sandu et al.,

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1996) is used for the integration of the set of stiff differential equations. KPP provides a variety of solver algorithms and it is freely available under the GNU license. We will add the references in the revised version of the manuscript.

5. We conducted some tests to evaluate the differences of the OH concentrations between the evaluation simulation $S1$ and simulations $E1$ and $E2$. The modification applied (i.e., the inclusion of $C_4 - C_5$ hydrocarbons decomposition) does hardly affect OH. In the chemical mechanism used in the model, the $C_4 - C_5$ hydrocarbons are responsible (all together) of at maximum $\simeq 10\%$ of the total OH sink, but generally below $\simeq 5\%$. Hence, although the alkanes distributions are different between $S1$, $E1$ and $E2$, their effect on the total OH concentration, is marginal. This is further confirmed by the fact that the maximum difference between simulations $S1$ and $E1$ in OH concentrations in the troposphere is $\sim 15\%$ during the simulated years. Moreover, the differences of monthly averages are much lower, less than 5%. Finally, no significant differences in the OH concentrations are present between simulations $E1$ and $E2$, with a maximum difference below 7%, which is reduced to less than 2% if the zonal average is considered. In conclusion, we confirm that the OH mixing ratio between the different simulations is different. However, these differences are relatively low and we can hence confirm that the OH fields are very similar between all the three simulations analyzed in the manuscript.
6. Following the question of the referee, we will reformulate the sentence. In fact, the ethane and propane mixing ratios are not independent on the emissions of the C_4-C_5 species. The OH concentrations are slightly modified by different butanes or pentanes emissions. This implies that all the other tracers which interact with OH are consequently modified. Nevertheless, as mentioned previously, the OH concentrations are only slightly changed between simulation $E1$ and $E2$. In addition the transport is very similar between the two simulations, due to the nudging (see above). Hence the ethane and propane distribution in simulation $E1$ and $E2$,

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although not binary identical, present negligible differences, which are not statistically significant. We hence decided to show only one of the two simulations in order to avoid very chaotic figures which would not add any new information.

7. We will remove the reference to Sect. 1, because indeed there is no information on the seasonal cycle of C_4 - C_5 hydrocarbons.

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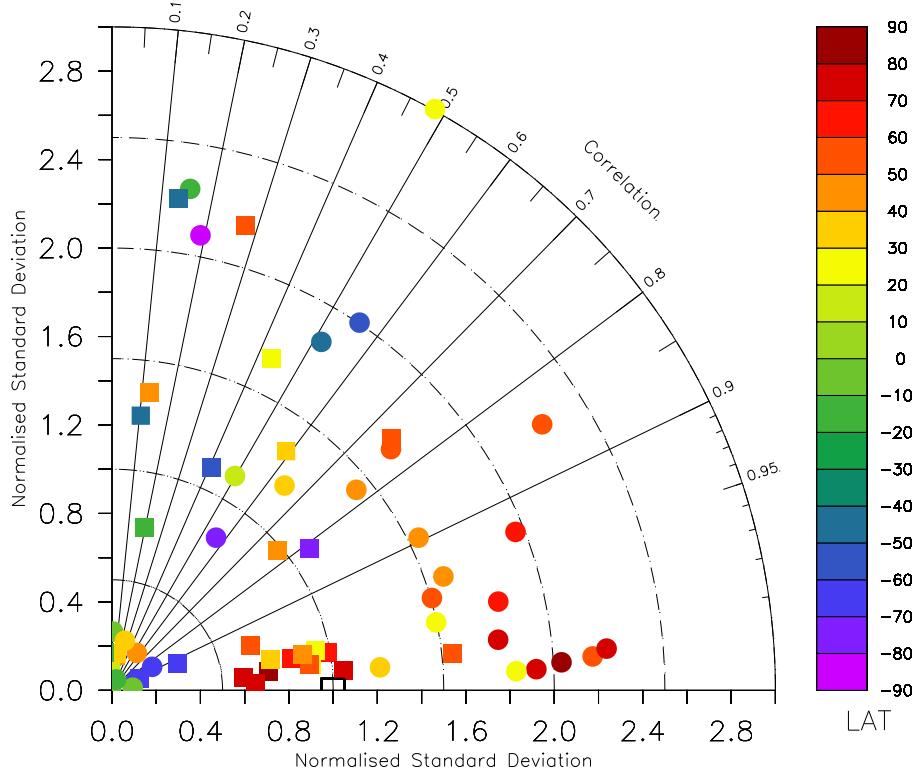


Fig. 1. Taylor diagram of C4H10. The colour code denotes the geographic latitude. The shape denote the model results used in the comparison: circle from simulation E1, square from simulation E2.

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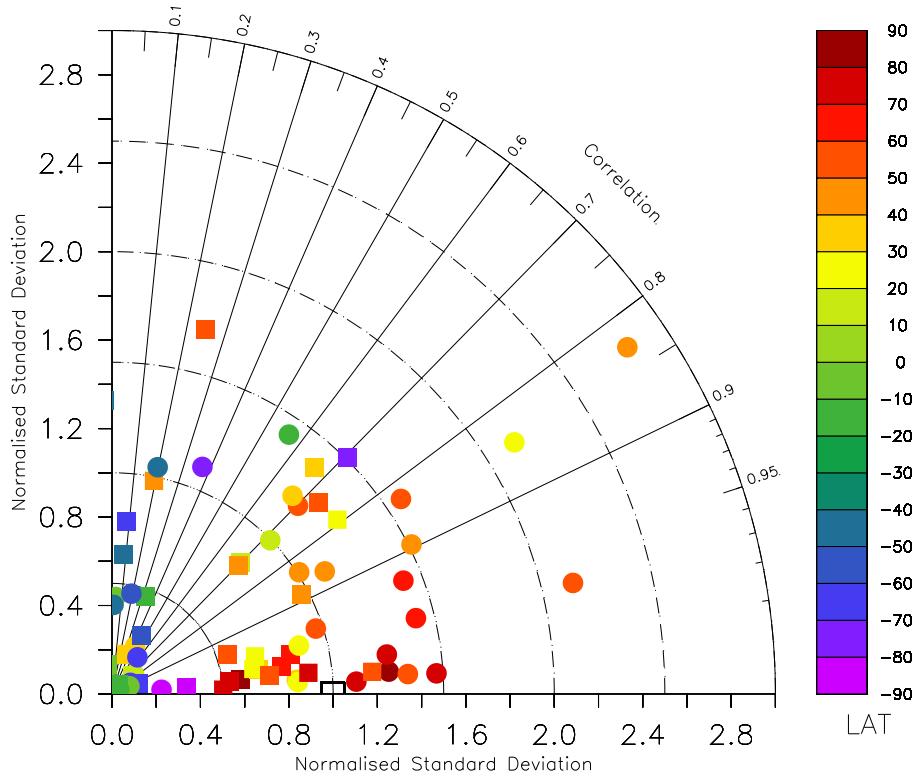


Fig. 2. Taylor diagram of I-C4H10. The colour code denotes the geographic latitude. The shape denote the model results used in the comparison: circle from simulation E1, square from simulation E2.

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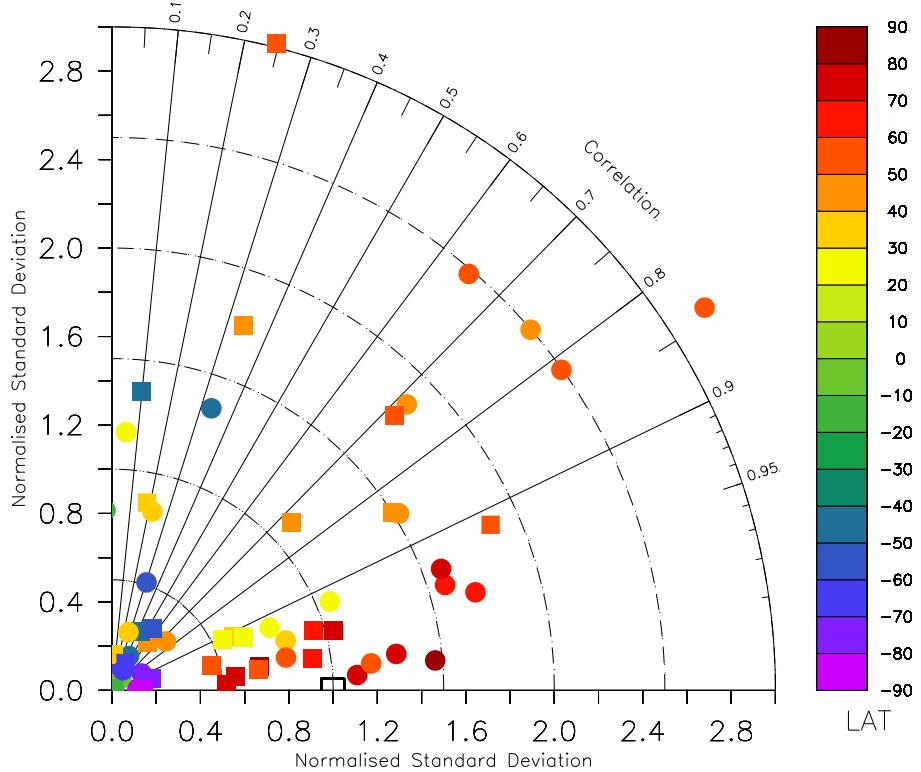


Fig. 3. Taylor diagram of C5H12. The colour code denotes the geographic latitude. The shape denote the model results used in the comparison: circle from simulation E1, square from simulation E2.

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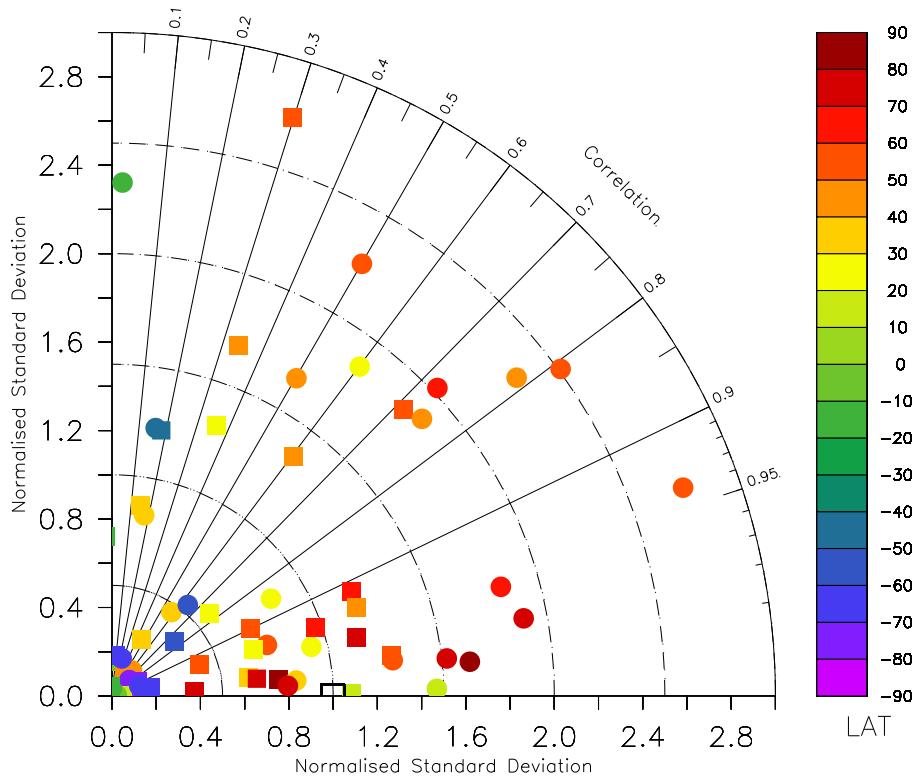


Fig. 4. Taylor diagram of I-C5H12. The colour code denotes the geographic latitude. The shape denote the model results used in the comparison: circle from simulation E1, square from simulation E2.

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