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Atmospheric Chemistry and Physics Discussions

Interactive comment on “Observed and simulated global distribution and budget of atmospheric $C_2{-}C_5$ alkanes” *by* A. Pozzer et al.

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We thank the anonymous referee #1 for the positive and constructive comments, which will help to correct some imprecisions in the manuscript.

We agree that a literature summary about the estimate of the global budget of acetone and acetaldehyde gives a better overview of the relative importance of the alkenes oxidation on these tracers. Although the text contains some informations about the budget of acetone on page 629, line 23, indeed a reference for acetaldehyde is missing. We will extend this part of the manuscript (and the introduction as well), adding more information on the importance of the alkanes oxidation on the budget of these two tracers. Nevertheless, we are reluctant in further discussing other sources of these tracers, because their large uncertainties require a much more sophisticated study,

which is well beyond the scope of this one (see also reply to minor comment 5)

Reply to specific comments:

1. We agree that the iso-butane emissions on page 620 are not coherent with the Jacob et al. (2002) emissions, and we thank the referee for discovering this erroneous calculation. Simulation S2 was indeed performed with 3.6 Tg C /yr i-butane (i.e., 4.35 Tg (i-butane)/yr). We will correct the text and provide the quantity in both units for coherence with Jacob et al. (2002). In addition, the text referring to this amount (as example on page 621,lines 4-10) and the table 1 will be corrected accordingly.
2. The references in the paper have been made to review the importance of acetone for the upper troposphere. We agree that recent studies modified such estimates. However, some of these were cited in the paper (see page 632 line 5 and 6, regarding the quantum yield (QY) estimate). Nevertheless, we agree that this was not underlined sufficiently. We will hence include in the revised version more up-to-date references (as Blitz et al. (2004) and Arnold et al. (2005)) showing that recent research unraveled a decreased influence of acetone in the upper troposphere. This was also confirmed in a previous paper using the same model (Pozzer et al., 2007), where the update QY was used.
3. We admit that the text is not precise here and deserves further clarification. Although we stated that the reaction products represent the "final degradation" products, these are tracers which are present in the chemical mechanism used in the model (i.e. without intermediate and additional tracers). However, some of these products (e.g., the peroxides) can still degrade and produce again acetone and acetaldehyde. This is the case for PrO_2 and EtO_2, which produce acetone

and acetaldehyde, respectively. The yield of acetone and acetaldehyde from alkanes must hence be calculated not only for the "direct" creation of acetone (following the alkanes + OH reaction), but must also include the further decomposition of the created peroxides. Hence, in our chemical mechanism the yield of acetone is ∼99 % from i-butane and ∼90 % for i-pentane. For acetaldehyde a yield of 0.44, 0.52 and 0.99 is calculated from n-butane, n-pentane and i-pentane, respectively. We will reformulate the text, adding these information and clarifying how the "yield" has been calculated. Finally the typo of the reported yield from Jacob et al. (2002) will be corrected (0.53 instead of 0.52).

4. From the model calculation, the oxidation of ethane leads to a creation of ∼ 18.1 Tg/yr of acetaldehyde. We did not include the oxidation of this tracer, because it was not an original part of the applied chemical mechanism (see as example von Kuhlmann (2001) or von Kuhlmann et al. (2003)). However, we completely agree that this is an important term in the acetaldehyde budget and its inclusion likely yields a more complete overview of the overall acetaldehyde production.

5. As indicated above, we agree in adding further text which can better explain the importance of the alkenes oxidation in the budget of acetone and acetaldehyde. Based on the literature, the alkenes oxidation contributes ∼20-25% of the total acetone sources (Jacob et al. (2002) and Singh et al. (2004)). Similarly, the alkenes oxidation is responsible for ∼ 15-19 % of the total acetaldehyde emissions (Singh et al., 2004), or ∼20-27% based on a more recent estimate (Millet et al., 2009). However, we are reluctant to start a discussion on the different sources of these species or to derive an estimate of the global budget. In fact, recent studies have modified drastically the overall budget of acetone from the estimates of Jacob et al. (2002). As example, while the ocean was considered a net emitter of acetone (see Jacob et al. (2002)), it is now thought that acetone has a net sink in the ocean (Singh et al. (2004), Marandino et al. (2005) and Taddei et al. (2009)). The lack of emissions from the ocean in the budget, however,

is partially compensated by changing two main terms in the acetone budget:

   - photolysis: as mentioned before (see item 2) the reduced QY leads to a reduced photodissociation and hence an increase of the acetone concentration (effect mainly in the upper troposphere).
   - biogenic emissions: as pointed out by Singh et al. (2004) (see also references therein), new measurements suggest a higher biogenic emissions than the one proposed by Jacob et al. (2002) (33 Tg/yr). Based on the modeling work of Potter et al. (2003), the biogenic emissions should be in the range of 50-170 Tg/yr.

   Similarly, also for acetaldehyde, there is still no agreement on the importance of the oceanic emissions (see as example Millet et al. (2009), and its open discussion).

   Because there is still a debate in the literature regarding the relative importance of the different sources with respect to the global emissions, we are reluctant in adding these informations which would require a detailed analysis. We will however include these references in order to give a better overview of the status of knowledge of the acetone and acetaldehyde budget.

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