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Atmospheric Chemistry and Physics Discussions

Interactive comment on "Characterization of non-methane hydrocarbons in Asian summer monsoon outflow observed by the CARIBIC aircraft" *by* A. K. Baker et al.

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We would like to express our gratitude to the referees for taking the time to review our manuscript and for providing us with detailed and constructive comments, which greatly help us in improving the manuscript. In light of the similarity of many of the comments we have opted to reply to all reviewers in a single document. Below we have given our responses to the referee comments; replies immediately follow the corresponding referee comments.

Response to Referee #1

Specific Comments

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Interactive Discussion

Discussion Paper

Comment 1. The background of the Asian monsoon circulation and how it affects the transport in the broad region of Southeast Asia is well described in the introduction. However, it seems to me that the definition and/or background of the monsoon outflow needs to be addressed more clearly in this study. For example, a regional map showing the location of the anticyclone, seasonal mean circulation showing strong easterly and westerly flows, the location of deep convection, and biomass burning activities will be very useful to be included in this work. Figure 2 does not seem to be very useful in this regard since the westerly flow in the high latitudes seems to be very prominent.

Reply: In light of your comments and the comments of the editor it is evident that Figure 2 needs to be revised. Therefore it has been modified accordingly for the revised manuscript with a clearer representation of the circulation. A second panel has been added to the figure which contains backward trajectories for air samples collected in August as well as a satellite image of cloud cover prior to the August flight indicating the regions of convection (see also responses to comments 3 and 5). Biomass and biofuel burning activities are more difficult to represent, as inventories are limited, although we note here and in the text that the burning of biofuel is widespread over the Indian subcontinent as described, for example, by Streets et al. (2003), Yevich and Logan (2003) and Ohara et al. (2007).

Comment 2. It would be useful to have some other comparisons. How about the flight paths from Frankfurt to other Asian countries, such as, China and Philippines?

Reply: It had been our original hope to be able to compare to data from CARIBIC's East Asian flight routes, as measurements of NMHCs in the UT/LS region covering an appropriately long period of time (the monsoon season plus at least a month before and after) are not available outside of data from CARIBIC. Unfortunately, measurements of NMHCs on the flights to China and the Philippines are very limited, with the monsoon months (June-September) being the most poorly covered. No measurements were made in September of any year, and the single June, July and August flights were in different years, ultimately resulting in a poor basis for comparison. Additionally,

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acetylene measurements, which were very integral to the analysis of monsoon data, were not made until 2008, when the flights to East Asia were discontinued. Lastly, we note that our measurements of other trace gases in this region also show monsoon influence and would potentially have shown the same for the NMHCs, making a poor comparison for consideration of background values.

Comment 3. The authors have concluded that the enhancements in the tracers are related to convective uplifts and biofuel burnings. A climatological map of convective uplift and inventory of biomass/biofuel will be necessary to support the conclusion.

Reply: Here we refer to our response to comment #1, where this has been addressed in part. Additionally, in the revised text we have used cloud cover analysis from satellite measurements to further support our conclusion of convection as the primary means of transport to the UT, and that this is further supported by the meteorological and chemical analyses of the monsoon and related convection referred to in the text (e.g. Devasthale and Gueglistaler, 2010; Fujinami and Yasunari, 2004; Park et al., 2009). Regarding biomass and biofuel burning, detailed information for this region is limited; however, we reference the work of Streets et al. (2003), and references therein, with regards to the low incidence of open biomass burning (which is primarily the burning of crop residues, which occurs after the monsoon season) during the rainy monsoon period and the widespread use of biofuels in the region.

Comment 4. It is mentioned in section 3 that the biomass burning is expected to be low since it is rainy monsoon season. Is there any wash out effect in the tracers due to rain?

Reply: Although we note that washout can be problematic for a number of atmospherically relevant species, for the compounds considered here very low solubilities result in the wash out effects being negligible.

Comment 5. I think the back trajectory calculations are very useful in this study. And some trajectory statistics (or a map) showing transport times adjacent to the monsoon

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outflow would be very useful.

Reply: Based on your comments and those of the other reviewers we have included a back trajectory panel for the August samples in the revised version of Figure 2 in the manuscript. We also note here and in the text that all CARIBIC backward trajectories are available at the KNMI website for the CARIBIC project, http://www.knmi.nl/samenw/campaign_support/CARIBIC/

Comment 6. In section 6 first paragraph – 1) Research flights should be replaced by commercial aircrafts. And 2) measurements in the monsoon outflow (if it is defined this way) would be more appropriate than within the Asian monsoon circulation.

Reply: "Monthly research flights" been changed to simply read "monthly flights". We have opted to keep the phrase as "within the Asian monsoon circulation", as this phrase describes the general location of the CARIBIC aircraft during these flights.

Technical Comments

Comment 1. There are three Liu et al. (2009) papers in the references. They need to be distinguishable.

Reply: Thank you very much for pointing this out – the first two Liu papers are not quoted in the manuscript and remain from an earlier version. They have now been removed.

Comment 2. Figure 1 – It is not mentioned that what the dots and solid lines mean.

Reply: Definitions of each have been added to the figure caption (dots = sampling points, solid lines = flight paths).

Comment 3. Figure 4 – It would be more interesting if fewer species with stronger gradient and other months were included rather than only for summer for better comparisons.

Reply: For the sake of completeness and comparability to the compounds shown in

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Figure 3 we chose to keep all compounds in the figure.

Response to Referee #2

Specific Comments

Comment 1. Biofuel burning is one of the major sources of anthropogenic pollution in SoutheastAsia, as clearly pointed out in the paper. Hence, whenever possible, observations of NMHCs should be supported by observations of the biomass burning tracers CH3Cl and CH3CN. The CARABIC instrument package includes these observations (see e.g. Lai et al., ACP, 2010) so the authors should use these data in their analysis when they are available or give a valid explanation why they do or cannot use these data in the present study (e.g. due to a mal-functioning instrument).

Reply: Data from the PTR-MS are not available for July, and the high level of noise in the August real-time CH3CN data makes determination of the biofuel burning influence and signature through comparison to CO difficult. Integration of real-time data to the TRAC sampling periods reduced the noise, but resulted in only four points where the NMHC and CH3CN measurements overlapped during the sampling periods used for the signature. Given these limitations we were not able to use CH3CN for the analysis. Methyl chloride was not analyzed during all months of the monsoon period, making it difficult to apply the same analysis to CH3Cl as to the NMHCs (particularly when defining the background/non-monsoon mixing ratios. Considering the difficulty applying the NMHC analysis to the more limited CH3Cl data set, and also given the fact that a paper discussing the halocarbons is planned, we decided against the use of CH3Cl in this manuscript.

Comment 2. The authors refer to NMHCs enhancements during summer relative to spring and fall. Similar to the comment of referee #1 I believe that it would be very useful to compare the absolute data of this study with measurement data from neighboring areas. How important are these enhancements in absolute sense as compared to comparable studies? I would suggest comparing the data of this study in any case

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with those in the recently published CARABIC paper by Lai et al. focusing on South China and the Philippines.

Reply: As mentioned in the reply to referee #1, who also inquired about a comparison to CARIBIC data in SE Asia, the summer months were poorly covered by these flights and data availability is too limited to make a meaningful comparison. To our knowledge no other datasets exist that would make for reasonable comparisons to CARIBIC data, as regular UT measurements of NMHCs are rare to begin with.

Comment 3. The potential role of enhancement NMHCs as precursors for ozone formation is mentioned in the conclusions as one of the chief concerns of monsoon outflow without having addressed this topic in further detail earlier in the paper. The authors should try to address this phenomenon in more detail in the Results and Discussion, e.g. using the ozone data as well as the dO3/dCO ratios from the same flights and comparing these with results from other studies that focus on Asian outflow (e.g. like in Lai et al., 2010).

Reply: In light of your and other comments we have added a discussion of the relationship between ozone and the NMHCs as well as photochemical tendencies to the manuscript. We also would like to mention that the structure of ozone in the plume is described in greater detail in Schuck et al., 2010. Overall we see a negative correlation between ozone and NMHC ratios that indicates ozone is being formed in the air parcels. However, in the north, where air parcels are more aged, there is no clear relationship, but due to the greater potential for intrusion of stratospheric ozone at higher latitudes, it is not possible for us to determine whether or not this is the result of the air parcels' reduced tendency for ozone formation, or to enhanced ozone due to stratospheric influence.

Technical comments

Comment: Abstract, line: replace "...that included the non-methane hydrocarbons." by ". . . that included a number of C2-C8 non-methane hydrocarbons."

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Reply: The recommended change has been made.

Comment: p. 18103, line 16: ". . . and lower stratosphere." please add a reference here.

Reply: A reference to Randel et al., 2010 has been added to the manuscript.

Comment: p. 18107, line 14-15: ". . . mixture of NMHCs purchased from the National Physical Laboratory (NPL, United Kingdom)." Please add a sentence on the accuracy of your standards here.

Reply: The accuracy of the standard (2%) has been added to the text here.

Comment: p. 18109, paragraph 3.1, comments on the first sentence on the role of OH. Note that this is mainly true for mid- and high-latitude and to a lesser extend for the (sub)-tropical regions were seasonal variations are more transport driven.

Reply: This is a very good point, and we have rewritten the sentence to make this latitudinal dependence more clear.

Comment: p. 18116, line 23, the authors use an estimated [OH] value of 2.4810 x 106 molec cm−3. This is an model estimated value and should not be presented with four digits. Write 2.48 x 106 molec cm−3 and try to give an uncertainty here.

Reply: This is actually a typo, and thank you very much for catching it! The value given in the referenced text is 2.48x106 molec cm-3, and the superfluous 1 and 0 have been removed from the value we quote. Also, the uncertainty has been noted in the revised text.

Comment: p. 18117, line 22, also here try to give an uncertainty value to the estimated [OH] of 1.44 x 106 molec cm−3.

Reply: The uncertainty of the OH estimate from Spivakovsky et al (2000) is noted in the revised version of the text, along with the related uncertainties in the estimated photochemical ages (please see response to referee #3).

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Response to Referee #3

General Comments:

Comment: The paper should make better use of all the other measurements from CARIBIC. The importance for ozone production is discussed, but no ozone data are shown. What is the ozone inside the monsoon outflow and what is observed in other places and times? How does this change the oxidative capacity of the atmosphere? Also I thought the CARIBIC package includes a PTR-MS and measurements of the biomass burning marker acetonitrile should be available. This would greatly improve the source identification of biofuel burning versus anthropogenic/urban sources or LPG.

Reply: As mentioned in our reply to referee #2 (comment 3), we have added a discussion of the relationship between the NMHCs and ozone to the manuscript. Regarding acetonitrile, we unable to use this data for the analysis for reasons described in our response to comment 1 of Referee #2.

Comment: I am surprised by the strong enhancements of i-butane and n-butane compared to the other small NMHCs. Also ethane enhancements are somewhat larger than expected from the comparison to other measurements, but propane not as much. The authors conclude that there are additional sources due to the use of natural gas and LPG and that this source is increasing over the past 10 years. Natural gas is usually mainly composed of ethane and LPG mainly of propane. If natural gas and LPG use were the main source for i-butane and n-butane, ethane and propane should be even more enhanced. Besides combustion sources, gasoline evaporation is a very strong source of i-butane and n-butane together with i-pentane. I would suggest looking at the enhancements (possibly age corrected) of those five compounds together and compare those carefully to source profiles of all evaporative and combustion sources to see, if they are consistent with the strong propane source from LPG and natural gas use.

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Reply: This is a very interesting point. We attribute the relatively large enhancements in the butanes in part to their much shorter lifetimes (and therefore much smaller background concentrations). And we also failed to discuss the potential influence of gasoline evaporation as a source, which would indeed contribute to larger enhancements in the butanes than in ethane and propane. Unfortunately, levels of i-pentane frequently near or below the detection limit make its use as a tracer difficult and somewhat limit the discussion. However, in the revised text we have expanded the discussion of ethane, propane and butane enhancements to include the potential contribution of gasoline evaporation.

Comment: I would like to see a better error estimate of the airmass age calculation. The different samples give ages between 3-8 days, which is a rather wide range. There are large errors associated with the use of climatological OH (Spivakovsky et 2000), mixing with ambient air (described in Figure 7) and the use of emission ratios estimated from the ground measurements. The uncertainties for all those should be clearly explained and the combined error estimate should be given and compared to the range of ages that are calculated.

Reply: There are certainly very large errors associated with age estimates that rely on estimated OH and emission ratios, and in the original version of the text we did not make it clear the effect that these would have. In the revised version we have endeavored to clarify these uncertainties. The uncertainties associated with each estimate are more clearly stated and discussed, along with the effect errors in each have on the estimated age. We also give an error estimate for the age calculations given in the manuscript.

Minor comments:

Comment: Page 18105: line 1: OH abbreviation should be given here not on line 8. Also see page 18109 line4.; Page 18104: line3: typo: there exists; Page 18107 line20: typo: and these sampled through the same inlet

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Reply: The corrections stated above have been made to the revised manuscript.

Comment: Table 1: it would be good to add CO here, especially the appropriate kOH.

Reply: We have added information for our CO measurement, as well as the kOH, to Table 1.

Comment: Table 3: typo: propane/CO also why is there no age corrected value for propane?

Reply: The typo has been corrected and the age corrected value for propane from the CARIBIC samples (which was shifted by one cell) has been added to the Table. We note here that no age corrected value for propane/CO was given in de Gouw et. al (2001) due to poor correlation between the two compounds.

Comment: Figure 4: I think it would be better to show all the data points for the butanes and pentanes.

Reply: It would have been our preference to show all data points, as well. However, rescaling the axes for the inclusion of the very high butane and pentane values (from a single point) made it difficult to see the latitudinal trend in these compounds, which is the justification behind drawing the points off-scale.

References

Devasthale, A. and Fueglistaler, S.: A climatological perspective of deep convection penetrating the TTL during the Indian summer monsoon from the AVHRR and MODIS instruments, Atmos. Chem. Phys., 10, 4573-4582, doi:10.5194/acp-10-4573-2010, 2010.

Fujinami, H. and Yasunari, T.: Submonthly Variability of Convection and Circulation over and around the Tibetan Plateau during the Boreal Summer, J. Meteor. Soc. Japan, 82, 1545–1564, 2004.

Lawrence, M. G. and Lelieveld, J.: Atmospheric pollutant outflow from Southern Asia:

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10, C10121–C10131, 2010

a review, Atmos. Chem. Phys. Discuss., 10, 9463-9646, 2010.

Ohara, T., Akimoto, H., Kurokawa, J., Horii, N., Yamaji, K., Yan, X., and Hayasaka, T.: An Asian emission inventory of anthropogenic emission sources for the period 1980–2020, Atmos. Chem. Phys., 7, 4419-4444, doi:10.5194/acp-7-4419-2007, 2007.

Park, M., Randel, W. J., Kinnison, D. E., Garcia, R. R., and Choi, W.: Seasonal variation of methane, water vapor, and nitrogen oxides near the tropopause: Satellite observations and model simulations, J. Geophys. Res., 109, D3302, doi:10.1029/2003JD003706, 2004. Schuck, T. J., Brenninkmeijer, C. A. M., Baker, A. K., Slemr, F., von Velthoven, P. F. J., and Zahn, A.: Greenhouse gas relationships in the Indian summer monsoon plume measured by the CARIBIC passenger aircraft, Atmos. Chem. Phys., 10, 3965-3984, doi:10.5194/acp-10-3965-2010, 2010.

Streets, D. G., Bond, T. C., Carmicheal, G. R., Fernandes, S. D., Fu, Q., He, D., Klimont, Z., Nelson, S. M., Tsai, N. Y., Wang, M. Q., Woo, J. –H., and Yarber, K. F.: An inventory of gaseous and primary aerosol emissions in Asia in the year 2000, J. Geophys. Res., 108(D21), 8809, doi:10.1029/2002JD003093, 2003.

Yevich, R. and Logan, J. A.: An assessment of biofuel use and burning of agricultural waste in the developing world. Global Biogeochemical Cycles, 17, 1095, doi:10.1029/202GB001952, 2003.

Interactive comment on Atmos. Chem. Phys. Discuss., 10, 18101, 2010.