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Atmospheric Chemistry and Physics Discussions

Interactive comment on "Increasing concentrations of dichloromethane, CH₂Cl₂, inferred from CARIBIC air samples collected 1998–2012" *by* E. C. Leedham Elvidge et al.

Anonymous Referee #2

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This manuscript presents measurements of CH2Cl2 obtained at 10-12 km altitude from 1998 to 2012 from CARIBIC observatory, and provides discussion about recent increase in the atmospheric trend in comparison with previous studies. From the extensive data sets covering various northern hemispheric regions, authors attempt to quantify regional emission sources, suggesting possible anthropogenic uses of CH2Cl2. There is a lot of interest in the CARIBIC project and its decent data, and this paper contains significant material and merits publication in Atmospheric Chemistry and Physics after the following discussions are considered.

General comments:

1. "Introduction" needs to be more organized to focus on the issues authors want to address in this manuscript; physico-chemical properties of CH2Cl2, its environmental significance, overviews of long-term trend and NH-SH gradient based on the previous records, and recent changes inferred from ground measurements in the trend would be stated before introducing what additions could be made to recent findings by flight observations like CARIBIC campaign. Then authors specify questions that they deal with based on their data sets. It would also be helpful if brief description about the following sections or guide on the rest of the manuscript were given at the end of the "Introduction".

2. It will be easier to read if the "Methods" section is divided into following subsections: 2.1 Whole Air Sampling, 2.2 Halocarbon Measurement Systems (2.2.1 Instrumentation 2.2.2 Measurement Precision 2.2.3 Calibration), 2.3 Ozone and Carbon Monoxide, 2.4 Back Trajectories.

3. In "Results and Discussion", data from four regions of Europe, South Africa, India, and the North and Central Atlantic were selected for each subsection. Explanatory titles of the subsections can be given instead of the regional names to describe different issues of each regional data set.

4. One major point I would like to see discussed more quantitatively in this manuscript is statistical significance of the temporal increase in the European time series and of latitudinal gradients in the flights to South Africa. Since the data intervals were not even with time and latitude, temporal and spatial binning should be examined very carefully. In addition, comparisons with the previous measurements should be made considering not only complexity of CARIBIC flight tracks, but also seasonality, horizontal and vertical gradients of CH2Cl2 and its year-to-year variations in atmospheric trend.

5. Another issue is regarding more quantitative justification of air masses from the Indian subcontinent to ensure convective isolation from the southeast Asian region

during the Asian Monsoon and thus the annual emission estimates from the Indian region.

6. One of main conclusions in this manuscript was that recent increase in the atmospheric concentration of CH2Cl2, which was discussed from CARIBIC flights over the European and Indian regions, “must be linked to” increasing use of CH2Cl2 as a feedstock for the HFC-32 production. However, this conclusion should be stated with further investigations, since a recent study by Li et al. (EST, 2014) demonstrated that in China, the world’s largest consumer of CH2Cl2, it had been used mainly as solvent in chemical manufacturing industry, and interestingly not shared the same emission source with HFC-32.

Specific comments:

1. P20723, LN 2-3: References are needed.

2. P20724, LN 9-10: Significance of contribution of VSLS at 10-12 km to the stratospheric chlorine amounts depends on the latitude, and thus this sentence seems to be valid only in the TTL.

3. P20724, LN 10: Please provide references for the sentence saying “CHCl3 is of predominantly natural origin”. Also consider other study, done by Aucott et al. (JGR, 1999), arguing that at least 50% of CHCl3 emitted in the NH were originated from anthropogenic sources.

4. P20728, LN 25-27: References are needed.

5. P20728, LN 28-29: To exclude the stratospherically-influenced air masses more accurately, it would be better to examine O3, a stratospheric tracer in combination with CO data as a tropospheric tracer.

6. P20730, LN 11: Back trajectories of the air masses in discussion can be provided to illustrate their geographical sources.

7. P20730, LN 28: Isn’t there any discernible latitudinal gradient from Barrow to Mace Head?

8. P20731, LN 19: Uncertainty of the averages over Canada and Greenland should be given for comparison with the mean in 2008 of the CARIBIC European data.

9. P20731, LN 25: Please add the reason why 30°N was selected as a latitudinal boundary. It seems a bit arbitrary. For the consistency with the rest of the manuscript defining the tropical band between 25°S to 25°N, 25°N would be a better boundary.

10. P20732, LN 1-3: References are needed. Otherwise, the argument that observed increase in latitudinal gradient implies increase in NH industrial activities associated with CH2Cl seems less convincing.

11. P20732, LN 20-24: Please state the sampling seasons to show the data from the CARIBIC flight tracks to South Africa covered possible biomass burning periods.

12. P20733, LN 11: Y-axis scales of Figures 4(a)–(e) should be all identical for comparison.

13. P20734, LN 20-24: Please add the references for these statements. Otherwise, more quantitative analysis should be made for further discussion.

14. P20735, LN 1: ’data us’ should be replaced with ’use’

15. P20735, LN 4-6: how can we justify that 35 samples < 40°N were originated only from the Indian subcontinent, not from the Southeastern Asia? Is it possible to investigate the back trajectories for the 35 samples?

16. P20736, LN 15-17: Please compare a CH2Cl2-CO ratio for the air masses influenced predominantly by the Southeast Asian region to rule out transport effect.

17. P20737, LN 15-20: These sentences are not properly stated. Age-correction for emission ratio is needed due to different loss rates between CH2Cl2 and CO (i.e., difference in chemical lifetime between CH2Cl2 and CO), which can cause apparent

change in their emission ratio after transit for a certain time interval.

18. P20738, LN 1-5: Please cite the references.
19. P20740, LN 12: Please specify the three previous studies.
20. P20741, LN 9: 'that' should be 'than'.
21. P20741, LN 23-26: References should be given.
22. P20742, LN 22: X-axis of Figures 8(a)-(e) should be identical.
23. P20743, LN 19-21: References should be given.

Interactive comment on Atmos. Chem. Phys. Discuss., 14, 20721, 2014.