Atmos. Chem. Phys. Discuss., 8, S5989–S5992, 2008
www.atmos-chem-phys-discuss.net/8/S5989/2008/

Atmospheric Chemistry and Physics Discussions

Interactive comment on "Contribution of very short-lived organic substances to stratospheric chlorine and bromine in the tropics – a case study" *by* J. C. Laube et al.

Anonymous Referee #1

Received and published: 14 August 2008

1 General Comments

The authors present data on a fairly complete suite of chlorine and bromine containing source gases measured in air samples taken in the tropical upper troposhere and stratosphere during a dedicated balloon flight. The measurements are performed using state of the art techniques and good accuracy is achieved on the measurements. Over all the study makes an important contribution to the understanding of total stratospheric Cl_y and Br_y which are key parameters for quantifying anthropogenic stratospheric ozone depletion. Especially the total stratospheric Br_y (and the contribution of

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VSLS and possibly product gases) is still not constrained very well and estimates range from 18 to 25 pptv, leaving too much of an uncertainty for any detailed study of chemical ozone depletion. The paper provides a very valuable new data set on chemical species which are not readily measured and where a lack of good data exists.

The structure of the paper seems a bit odd at places. Details of the measurement (location etc.) are given in the introduction while the quality assurance and the error budget are dealt with under section 3 Results and Discussion. It would be more natural to combine these parts in section 2 possibly with a modified section title so not to distract the reader in the discussion section.

Unfortunately several organic bromine species detected in the analysis could not be identified and therefore not quantified due to the nature of the measurement technique. However, the potential of these missing species to significantly increase (i.e. by several ppt) the determined bromine budget should be discussed in more detail. I.e. are there tropospheric measurements for the candidate species listed for some of the unidentified signals and what would they add up to?

In summary the paper should be revised within these two mentioned aspects and also on the points detailed below in order to be accepted for ACP.

2 Specific and Technical Comments

p.8492,l.21: BrONO2 also is an important stratospheric Br_y species and should be mentioned.

p.8493,l.1: A reference should be given for the relative efficiency to destroy ozone of bromine vs. chlorine.

p.8493,l.2: 0.1ppt bromine correspond to 6ppt of chlorine, i.e. 0.2% of Cl_y . I doubt that this amount is of any major importance for ozone depletion.

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p.8495,l1.4: The increase of species mixing ratios in the sample cylinders seems strange. This can only result from the decomposition of other species but products like CH_2ClCH_2Cl seem rather improbable? Also the nature of the "non-systematic processes" possibly leading to the build-up of CH_2Cl_2 in the high altitude samples should be detailed if possible. Have such effects been observed or studied in detail in any prior publications and, if yes, please cite these papers. It would also be interesting to see how consistent the observed increases are in different samples.

p.8496,l.5: A reference or at least web-site should be given for the NOAA-ESRL data.

p.8496,l.8: It should be clearly stated which species mixing ratios would most probably be significantly affected by the effect of local convection otherwise this statement seems rather unmotivated.

p.8496,l.22 and Fig.1: The trajectory calculation does not provide any information on the vertical motion of the probed air masses. Therefore the conclusion that the air originates from continental air masses from both hemispheres seems not valid without further arguments. Fig. 1 needs some work so the coast lines become more visible.

p.8501,l.20: The statement is trivial. The sharp increase of Cl_y above the tropopause is of course caused by decomposition of the shorter-lived species but it clearly shows that this air must be significantly older than the air in the TTL probably caused by the way the air enters the stratosphere. The modelling paper by Konopka et al. (ACP 2007) could be referenced here.

p.8501,l.28: The measurement by Dorf et al. has now been published in ACPD and this paper should be referenced.

p.8502,l.4: A reference for the AGAGE network should be given.

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