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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.

J. C. Laube et al.

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Referee comment(s)

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.

Author response

The structure of the manuscript was reworked to improve its readability. The men-

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tioned section of the introduction was moved to section 2 as a new subsection (2.1 Sampling techniques). Moreover, two additional subsections of section 2 were created (2.2 Measurement techniques and 2.3 Air mass origin – the latter was moved from section 3.1). The main part of section 3.1 (Quality assurance) does not fit to the Analytical procedures section nor to the discussion. Thus, a new section was created (3 Quality Assurance) which is subdivided into three subsections: 3.1 Concentration drift and blank corrections, 3.2 Intercomparison with ground-based observations and in addition 3.3 Error bar calculations (moved from former subsections 3.1 and 3.2).

Referee comment(s)

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?

Author response

To our knowledge there are no published global tropospheric time series for the listed candidate species up to now. Moreover, as mentioned in the manuscript, in NICI detection mode the size of a peak is not indicative for the substance’s concentration, which makes an estimate impossible. The intention of the authors was to stimulate further research by questioning the completeness of the list of brominated substances that are currently believed to reach the stratosphere.

Referee comment(s)

p.8492,l.21: BrONO2 also is an important stratospheric Bry 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.8496,l.5: A reference or at least web-site should be

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given for the NOAA-ESRL data. 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.

Author response

The manuscript was adapted as requested.

Referee comment(s)

0.1ppt bromine correspond to 6ppt of chlorine, i.e. 0.2% of Cly . I doubt that this amount is of any major importance for ozone depletion.

Author response

It is spoken of 0.1 ppt of brominated substances. In the case of bromoform this would correspond to 18 ppt of chlorine. The authors don’t see this as a negligible contribution.

Referee comment(s)

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 CH2ClCH2Cl seem rather improbable? Also the nature of the ”non-systematic processes” possibly leading to the build-up of CH2Cl2 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.

Author response

The new subsection 3.1 (Concentration drift and blank corrections) was expanded to provide evidence that such concentration changes are known and to inform the reader about possible causes: “It is a known problem that many organic trace gases drift in concentrations... caused by adsorption or chemical reactions e.g. on

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active spots of the container walls (Pate et al., 1992; Apel et al., 1994)…Positive changes with time have also been observed…” Moreover, information is now provided on the criterion for “systematic” and “non-systematic changes”: “If changes occurred in all containers that contained the substance they were assumed to be systematic if the mean percentage change exceeded the percentage 1σ standard deviation of the samples concentration changes. This means that the variability of the concentration changes did not exceed the changes itself.”

Referee comment(s)

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.

Author response

We agree that the VSLS would be affected most. The statement was adapted and hopefully appears more motivated now: “In combination with the observed low VSLS mixing ratios (see below) this indicates that a well mixed air mass with little influence from local deep convection was sampled (VSLS should be super-elevated in the case of convective influence).”

Referee comment(s)

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.

Author response

Information on vertical transport was added. Above the level of zero radiative heating the quasi-isentropic transport is realistic. We admit that below the calculations of

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vertical winds in the tropical upper troposphere are connected with high uncertainties. Therefore the continental air mass origin is questionable and this adjective (i.e. continental) was removed. However, all calculations showed an air mass origin from both hemispheres, which is why this statement seems reasonable to us. In addition the Figure 1 was reworked and the coast-lines are more visible now.

Referee comment(s)

p.8501,l.20: The statement is trivial. The sharp increase of Cly 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.

Author response

We agree with the referee that the observed sharp increase is trivial for experts but find it a good example to demonstrate the transition from troposphere to stratosphere to a broader scientific community. Moreover, from our point of view the presented case study data does not provide enough spatial resolution to draw conclusions about dynamics of the TTL. The stated sharp increase is mostly due to the rapid decomposition of CH3Cl and CCl4 and the statement was adapted to clarify.

Interactive comment on Atmos. Chem. Phys. Discuss., 8, 8491, 2008.