

Interactive comment on “Halogenated organic species over the tropical rainforest” by S. Gebhardt et al.

S. Gebhardt et al.

Received and published: 24 April 2008

We thank the reviewer for their thorough assessment of this manuscript and helpful suggestions. The comments and our replies are listed below.

Specific Major Comments:

1162 (11) and 1175 (17): "The statement about the methyl bromide's lifetime impacting the source-sink imbalance needs to be made quantitatively. I personally do not see that there is enough wiggle-room in methyl bromide's lifetime to be able to support a large budget closure (e.g. see J. J. Colman et al., 2001). If you believe this to be the case, please show the % deviation in methyl bromide's lifetime that you believe can occur, and then relate this to the quantitative amount by which it would then close the budget."

Reply: This statement is illustrated in a recent paper of A. Kerkweg, accepted for publication in ACPD (ACPD-2008-0095). The results of this study imply a 50% longer lifetime for CH₃Br, i.e. 386 days instead of 255 days referring to the latest Scientific Assessment of Ozone Depletion (WMO, 2007). This "new" -by a factor of 1.5- longer lifetime implies that the sinks are also smaller by a factor of 1.5 compared to prior estimated. Applying this factor to the CH₃Br global sinks estimates of 129 to 387 Tg/yr (WMO, 2003) results in a range of 86 to 258 Tg/yr. This is much closer to the given source range of 77 to 293 Tg/yr (WMO,2003).

1167 (11): "This interpretation uses words like "seemed" and "appears". It is important to know whether or not the variations with altitude are real, because they are the basis of the regional and global flux calculations that are presented. Use your statistics to show whether or not the trends are significant. Do the results change on a flight-by-flight basis? I would also like to see a figure that shows each individual data point vs. altitude, so we can see the scatter and what went into the Figure 4 plots. This will be especially useful for clarifying the LFT peaks for CH₃Cl (e.g. 1167 (27))."

Reply: The GABRIEL experiment was deliberately focused on the mixed layer, hence a large number of samples were taken in this height range. Unfortunately, the vertical structure above has relatively few data points. Thus our approach was to present the binned data averages and offer an interpretation of the profiles. From the revised Figure 4 it can be seen that the features described are not statistically significant (in contrast to the fluxes derived in the horizontal) and that we have over-interpreted this section. The relevant part on the manuscript was amended to read:

"The CH₃Cl profile showed higher mixing ratios near the ground decreasing with altitude. The average within the mixed layer was 643 pmol mol⁻¹, decreasing to 600 pmol mol⁻¹ within the LFT and further to 575 pmol mol⁻¹ on average in the FT; the one outlier (marked with a circle in Fig. 4) is discussed further below. The vertical distribution of CH₃Br was quite scattered, which is in part due to the 7.8 % precision error. The mixing ratios varied between 7.7 and 10.9 pmol mol⁻¹ showing no significant trend with

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height. The CHCl_3 profile showed a decrease in mixing ratio from ML (8.2 pmol mol⁻¹) to LFT (7.0 pmol mol⁻¹). The average FT values were again slightly elevated (7.5 pmol mol⁻¹). Taking into account the uncertainty of the data points no statistically significant information on the source distribution could be obtained from the vertical profiles. Nevertheless, on average higher mixed layer mixing ratios of CH_3Cl and CHCl_3 pointed to a ground based source of these compounds. This surface source is further investigated in section 3.4. The elevated value at 7.9 km visible in all three components corresponded to a sample taken within air strongly influenced by biomass burning. It coincided with elevated values in the biomass burning tracers carbon monoxide (CO) and acetonitrile (CH_3CN) (H. Bozem, personal communication)."

Nevertheless, the increasing methyl chloride and chloroform mixing ratios towards to surface point to a ground based source. This source is further evaluated in section 3.4. The variation with TOL, which is the basis for the regional and global flux calculation, is shown to be significant (see Fig. 5).

Figure 4 has been revised providing individual data points including their error bars.

1169 (9-23): "The arguments here need to be tightened. First, as stated above, it needs to be shown that the enhancement at 1-2 km was statistically significant. Next, how was it determined that the ML was influenced by entrainment of advected biomass burning air rather than another source? If biomass burning is the source, by how much would CHCl_3 have been expected to increase? By a detectable amount? What other sources may have caused CH_3Cl but not CHCl_3 to increase? Do the back trajectories at this altitude give any clues? Also, the statement that "in this case the methyl chloride concentration at 2-3 km was higher than at the top of the boundary layer" does not make sense to me, based on Figure 4."

Reply: Since we could not prove the perceived enhancement at 2 km to be statistically significant, a detailed interpretation of the vertical structure is no longer feasible. As a consequence our interpretation of possible entrainment from an upper layer to the

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mixed layer needs to be changed. We removed the paragraph regarding entrainment from the text and replaced it by:

”Since the vertical profile showed no statistically significant mixing ratio changes in the transition zone between ML and LFT, the influence of entrainment from upper layers of air is not taken into account in the following calculations.”

To be able to investigate the vertical structure and the influence of entrainment/boundary layer ventilation thoroughly, we recommend a higher density of samples particular in the 2 to 4 km region for future projects in this region.

1176 (9-12): A more in-depth discussion of the CHCl₃ results is needed. How do your results change our understanding of the contribution of CHCl₃ to global Cl?

Reply: As also suggested by reviewer 1, a comparison with the global budget is now implemented in the text. Since our measurements provide net sources including all processes occurring within the ecosystem rainforest, it is difficult to compare exact numbers. The different contributors of our net source might be already incorporated in the current source terms of the global budget. The following paragraph was amended respectively: ”When the CHCl₃ flux results are extrapolated to all tropical ecosystems, the result is a net flux of 56 (+23 2sigma) Gg yr⁻¹. This is between 5 and 10 % of the total sources, and as previously mentioned, it could be already incorporated in the soil source term.”

Specific Minor Comments:

Title: ”To more accurately reflect the scope of your paper and where the measurements were made, change the paper’s title to ”Halogenated organic species over the South American tropical rainforest”. In the conclusions you state very nicely and clearly that the derived fluxes are a net flux (1177, 8-10) and that they apply to the rainforest ecosystem (1177, 23-25). However this is not clear in the abstract and other parts of the text. These are important distinctions that need to be incorporated throughout the

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paper. For example, on 1160 (23), "global extrapolation" could mean all global forests, tropical forests or tropical rainforests. Be specific throughout the paper."

Reply: We agree about the reviewer's recommendation. To specify the area of our measurements the term "South American" was added to the title. The title of the Section 3.4 Net Fluxes and 3.5 Global Emissions were complemented by the phrase "from the tropical forest". The last paragraph of the abstract was completely rewritten following a recommendation of reviewer 1. It now includes the information that we calculated "the net flux from a tropical ecosystem to the planetary boundary layer".

1160 (9): "The definition of "transport times" as 1-2 days is too broad. There are many transport times in the atmosphere, especially through a vertical column like you are measuring. Specify what you mean."

Reply: The term "transport times" was changed to "advection time from the coast".

1162 (20): "When was the use of CHCl_3 in pulp and paper production reduced (what year?)."

Reply: Long term measurements of chloroform (Trudinger et al., 2004, Worton et al., 2006) show a clear maximum mixing ratio around 1990. The decrease after 1990 might be related to significant changes in the industry. Worton et al. (2006) suggest the changing trend in bleaching methods to be responsible for decreasing chloroform emissions. He uses number provided by (Alliance for Environmental Technology: Trends in world chemical bleached pulp production 1990-2001, <http://www.aet.org/reports/market/2001.pdf>, 2001) to prove that the percentage of global bleached chemical pulp production using elemental chlorine has decreased by more than a factor a 5, from ~95% in 1990 to ~17% in 2002, and that elemental chlorine free and totally chlorine free bleaching methods have increased by the respective amount over the same time frame. Whereas Trudinger et al. (2004) refer to generally "decreasing industrial sources" since 1990, because of process improvements and other sources. Nevertheless, chloroform is not "used" but "produced" by the pulp and

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paper industry. On reflection we decided to remove the sentence and add instead "1990", because it is not proven that a change in industrial processes alone could account for the declining trend.

1163 (14): "Reference the statement that there is regionally prevalent deep convection. You may wish to investigate what the results from the July 2007 TC4 experiment (conducted in a similar region) have shown."

Reply: Presently there is no citable paper on the meteorological conditions in Suriname during the GABRIEL campaign.

We note with interest that the TC4 experiment was conducted in a similar region. Unfortunately no publications on the results of this campaign could be found to reference.

To reference the statement of regionally prevalent deep convection, we added the following paragraph, though in the section 3.1 Meteorological Conditions: "The cloud conditions observed were typical of tropical regions. This includes the development of shallow cumulus clouds in the morning, occasionally transforming into cumulonimbus clouds and hence thunderstorm activity in the late afternoon, before proceeding to clear sky in the evening."

To reference the general statement of prevalent deep convection within the ITCZ, we now refer the reader to the meteorological textbook (Holton, 1992).

1164 (10): "Is there a technical paper about the sampling system that you can refer the reader to? If not, discuss how you have tested the cans for leaks, artifacts, etc."

Reply: We have not written a technical paper specifically on this sampler. As mentioned in the manuscript, storage tests on the canisters have been performed and are reported by (Colomb et al., 2006). They indicated that the investigated halocarbons are stable over 60 days under dry and humid conditions. A description of the sampling system and figure showing how it was constructed is included in Williams et al. (2007). This paper is now referenced to in the text. Regarding the leak testing we added the

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following sentence to the text: "Thorough leak testing was carried out prior to the flights by pressurizing the sampling system with helium and looking for leaks with a helium detector."

1166 (16): "I think you have mis-used the word "stable". During the daytime the meteorological conditions will be unstable, so "stable" is confusing. Use "constant" or some similar word. "

Reply: The reviewer is right. "Constant" is the accurate description of the prevailing weather situation. The term was replaced.

1166 (20): Why would surface friction cause the wind to veer?

Reply: In the northern hemisphere wind backs when it encounters a rough surface (i.e. friction increases). This is because as the friction increases, the speed and hence the coriolis force decreases. The coriolis force then no longer acts opposite to the pressure gradient force, but more in the direction of the geostrophic wind. In the northern hemisphere the coriolis force acts to move an air parcel to the right and hence the wind backs. The reviewer is, however, right to question this sentence as the wind will in fact back not veer closer to the ground. To prevent any confusion the term was replaced as follows: "Closer to the surface the wind weakened and turned to a more northeasterly direction as a result of the increased friction with the surface."

1167 (27): "Do you really mean the 2-3 km peak, or the maybe more pronounced 1-2 km peak? (see p. 1169). Please clarify."

Reply: The whole paragraph concerning entrainment was withdrawn (see reply p1169 (9-23)).

1168 (4): "It would be interesting to know where the back trajectories originated from for the biomass burning sample."

Reply: The respective sample was taken at about 7.5 km above the ocean. A thorough analysis of back trajectories for this part of the flight track was conducted by H. Bozem.

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He used the Model LAGRANTO to calculate 21-day-back trajectories of the respective area. These trajectories identify no clear source origin. A statistic on the starting points of the trajectories showed, that 57% originated in Africa, whereas only 2% stem from South America. (Heiko Bozem, pers. Com.). A paper focussing on this case study is in preparation by Bozem et al. In order to bring this extra information into the manuscript, we added the phrase: "most probably originating from a distant biomass burning event in Africa."

1168 (18): "You might consider changing "no" to "almost no"."

Reply: Done.

1170 (7-14): "Because CH₃Cl has a strong latitudinal gradient, your results should be directly compared to the lower latitudes (apples and apples) and not the global average (apples and oranges). In other words, it is not surprising that your values are higher than the global average, and so the presentation of this comparison should better reflect this. The same reasoning applies to CHCl₃."

Reply: The reviewers point is well taken. To emphasis the good agreement of our data with tropical average mixing ratios this paragrah was revised. "The mixing ratios in the boundary layer ranged from 546 to 724 (avg 643) pmol mol⁻¹ for CH₃Cl, 6.6 to 11.2 (avg 8.2) pmol mol⁻¹ for CHCl₃ and 7.9 to 9.9 (avg 8.8) pmol mol⁻¹ for CH₃Br. These are somewhat higher than the global mean value of 550+-30 pmol mol⁻¹ for CH₃Cl, which is expected since generally higher concentrations are reported at lower latitudes (WMO, 2007). For CHCl₃, the values reported here agree very well with the average mixing ratio for the SH tropics, 9.7 pmol mol⁻¹ (Khalil and Rasmussen, 1999)."

1170 (26): "Rather than stating "probably influenced" by anthropogenic emissions, do you have other urban tracers that you measured that would confirm this?"

Reply: There is no consistent pollution marker in all three of these samples. One point shows elevated mixing ratios in C₂Cl₄ and toluene another one elevated xylene

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values, respectively. The third one was removed because of its geographical proximity to exclude any possible influence from the airport plume. Since there is no consistent signature of an anthropogenic tracer, we prefer to leave the formulation as it is.

1171 (21-22): "There are too many significant figures for the mean pressure and temperature. The same comment applies to some of the linear fits cited in Figure 5."

Reply: The redundant significant numbers were removed.

1171 (26): "Add a comment on how this lowest detectable CH₃Br flux compares to global emissions. "

Reply: The following sentence was added: "The global extrapolation of the lowest detectable CH₃Br flux yields 17 (2sigma) Gg yr⁻¹. A source of this size would be a not negligible contribution to the global budget supplying between 6 and 22% of the total global sources."

1172 (1-3): "It seems that this statement of "few measurement studies" has been applied to studies that determined local fluxes, but your measurements could also be compared to other South American studies, e.g. the vertical profiles and global flux estimates of Blake et al. (1996) that were cited earlier."

Reply: The study of Blake et al. (1996) examines the emission of trace gases during biomass burning events. The profiles presented by Blake et al. over the Brazilian rainforest are of air masses that have recently encountered local biomass burning. The calculated emission rates quantify the contribution of biomass burning to the global budget. The aim of our study is to determine the fluxes from an unperturbed "non burning" rainforest, therefore we don't think it makes sense to compare these fluxes (apples and pears).

1176 (1):"Reference the statement that tropical forests account for nearly half of the global total."

Reply: This number is taken from Chapter 4 (Table 4-47) of the FAO: Forestry Paper

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140: Global Forest Resources Assessment 2000 (FRA 2000), Food and Agricultural Organization of the United Nations, 1-149, Rome, Italy, 2001. The reference was inserted.

1177 (5): "An airborne flux measurement is something different than what you did (you took airborne mixing ratios, from which fluxes were subsequently derived). Change to "airborne measurements". "

Reply: Done.

Table 1: "A much more descriptive caption is needed for Table 1. Also, change "subtotal" to "total" throughout. "

Reply: The caption was changed to "Table 1: Current best estimate of the sources and sinks of CH₃Cl, CH₃Br and CHCl₃" and "subtotal" was replaced by "total".

Technical Corrections: There are several issues related to grammar and clarity that need to be addressed. Once a chemical (e.g. "methyl chloride") has been introduced by its chemical formula (e.g. "CH₃Cl"), use the chemical formula throughout the paper (e.g. 1162 (5), etc.). The same applies to ITCZ.

Reply: Done

Throughout, organize your references chronologically then alphabetically (e.g. 1168 (11); 1169 (2); 1172 (2-3); 1173 (29); 1174 (3-4)).

Reply: Done.

1162 (15): Papers published in 2003 are not really "recent" anymore.

Reply: "recently" was removed.

Section 3.2: The verb tense switches back and forth from past to present in this section.

Reply: The tense is now consistent.

1171 (11-12): The use of dashes here is confusing because the first dash reads like a

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minus sign. Use brackets instead.

Reply: Done.

1171 (19): It's a small point, but try using "ug" instead of "g" and "pmol mol⁻¹" instead of "mol mol⁻¹", to be consistent with the rest of the paper.

Reply: Manuscript was checked for consistency.

1176 (15-19): This is a very awkward and confusing sentence. Try: "Taking into account the measurements of Scheeren et al. (2003) - which were carried out in the same region - and using the average flux of both studies, the..."

Reply: Done.

Suggested changes to improve grammar and clarity were done and lacking commas were added.

Interactive comment on Atmos. Chem. Phys. Discuss., 8, 1159, 2008.

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