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Atmospheric Chemistry and Physics Discussions

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

Anonymous Referee #1

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This paper describes aircraft-based flask measurements of methyl chloride (MeCl), methyl bromide (MeBr) and chloroform (CHCl3) over the rainforest of NE South America and how elevated mixing ratios of these gases in flasks collected from the planetary boundary layer (PBL) above the forest were used to estimate their net rainforest fluxes. Statistically significant correlations are presented between MeCl and CHCl3 mixing ratios and the amount of time sampled air masses had spent over the rainforest. These time-based mixing ratio increases are converted to net ecosystem fluxes by designating a boundary layer height, then calculating the flux necessary to match the "accumulation" rates in the PBL volume.

For the most part, the paper is clearly written and its content is suitable for ACP. In some instances the paper overstates its conclusions (see comments below), but my

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main comment is that it lacks a clear, up-front answer to the question: Does this paper suggest significant changes to the tropical source/sink budgets of the three gases ? I would like to see this question answered in the abstract, the answer developed throughout the paper, and the impacts addressed in the conclusions.

General Comments:

The authors use the term "emission fluxes" in this paper which in reality examines net ecosystem fluxes from the tropical rainforest. These net fluxes probably result from many competing sources and sinks within the ecosystem. This work estimates the net amounts of these gases exported from the forest canopy to the PBL above the canopy, not their "emission fluxes".

In view of the previous comment, I would prefer to see all the background information about rainforest and other competing (biomass burning, coastal ecosystem) sources and sinks in the introduction. For example, discussions of leaf and fungi and plant emissions (pg 1173-1174) should appear earlier to emphasize that the ecosystem flux for each gas is comprised of multiple sources/sinks. The reader would like to know early on what the potential processes are that might influence the net fluxes. In other words, tell the reader what we know (and how well we know it), what we don't know that your study can explore, then what you learned from the study and how it impacts what we think we already know.

The terminology "missing source(s)" needs clarification. The budgets of MeCl and MeBr are not out of balance if the very large uncertainties are considered. The premise of a "need" for additional sources (or sinks) in specific latitudinal ranges (e.g., tropics) arises from inverse models. The estimates for many sources/sinkes cover such a wide range of values that they can be increased or decreased until agreement with the models is reached. So, realistically, there may be sources/sinks that we currently don't know about ("missing" from the budgets), but more likely the sources/sinks already identified simply need adjustments.

ACPD
8, S133–S140, 2008

I'm curious as to what the uncertainties are in the time over land (TOL) calculations. If relatively large (as suspected given the uncertainties of back trajectories), and accounted for in the linear fits (Figure 5), these can significantly alter the slopes of fit lines. Standard linear regression accounts only for uncertainties in y-variables; adding uncertainties to the x-variables and performing orthogonal distance regressions (also called "generalized least squares") instead may considerably change the slope values (fluxes).

It is of interest to know if low-altitude samples collected off the coast were similar in composition to all those collected at the coast (TOL=0). In other words, were there significant marine and/or coastal source influences on samples that set the boundary conditions (TOL=0) for determining additional mixing ratio enhancements by the rainforest? This is especially important because you are fitting absolute mixing ratios against TOL, not the changes from the boundary conditions for each flight against TOL. For example, if near-coast mixing ratios of MeCl are elevated in some samples (due to coastal sources) but not in others (Figure 5), the TOL=0 boundary conditions are very different for those trajectories. I think this can be addressed by showing that off-coast mixing ratios are the same as TOL=0 mixing ratios (see next comment for Figure 5).

I find Figure 2 to be superfluous because the data can be described in a simple way in the text. Instead I would like to see the CO and CH3CN vertical profiles added to Figure 4, the actual data from 99 samples presented in Figure 4 instead of vertical bin means and medians and boxes and whiskers, and ML data for TOL $<$ 0 (ocean) added to Figure 5 (fits should still cover the range TOL $>$= 0). It needs to be clarified what is plotted against TOL in Figure 5 - individual sample data or some statistical bin averages?

Specific comments:

P1160 L5: Nowhere in the paper do you discuss forest "hydrocarbons" so this statement certainly doesn't belong in the abstract.

ACPD

8, S133–S140, 2008

P1160 L12: You estimate fluxes for one week in October 2005, not for "the long dry season".

P1160 L19: Here and throughout; differences between the March 1998 and October 2005 results cannot be used to address seasonal variations or lack thereof in net fluxes, nor do these flux values "confirm that the rainforest is a strong source" without providing a comparison to the global source budget.

P1161 L4: Specifying the atmospheric lifetimes of these three halocarbons (instead of a range) would support claims of their ODPs and the ratios of their ODPs (P1162 L5)

P1161 L6: Theory/knowledge of ozone depletion by halogenated source gases dates back to the 1970's, not the WMO 2003 report. Cite the historical paper(s) here.

P1162 L4: Be quantitative when possible; "Although 50-60 times less abundant than methyl chloride ...". With a shorter lifetime and lower abundance that methyl chloride, you may want to mention why the ODP for MeBr is 25 times that of MeCl.

P1162 L10: Again, how can you claim there is a "missing source" of 45 Gg yr-1 MeBr from this budget with its very large uncertainties? I don't think the purpose of your study was to identify a "missing" source, but to provide a large-scale assessment of the net rainforest fluxes of these gases that might impact the "best" estimates of their sources/sinks.

P1163 L5-8: This sentence is very confusing. Do you mean the total of all terrestrial sources should be in the 89-104 Gg yr-1 range, with half to 70% of these sources apportioned to the southern hemisphere? Doesn't the MeBr budget need additional sinks or decreased sources, not additional sources?

P1164: Here is a great place to mention that the mixing ratios of these three halocarbons were stable in canisters for at least 60 days (not much later on P1172), for that is an immediate question the reader has when reading this section. Also, mention whether or not samples were dried on collection - this can have some bearing on

ACPD

8, S133–S140, 2008

the stability of methyl halides in steel canisters. How much of the sample was cryo-trapped? Was the column temperature ramped or isothermal?

P1165 L5-6: In this paper you are using differences between mixing ratios over the coast and rainforest to calculate fluxes, so the absolute accuracy of measurements is much less critical than the precision of measurements (unless the inaccuracy is very, very large). In other words, you are looking at the changes in mixing ratios rather than the absolute mixing ratios themselves. Therefore, the reader is much more interested in the precision estimates for these measurements rather than their "total" uncertainties.

P1165 L17: What was the mixing ratio range of detector linearity?

P1166 L8: Additional information about the estimation of boundary layer height is needed here. From my knowledge, it is sometimes very difficult to determine this from temperature profiles alone. How was the relatively small uncertainty of the average boundary layer height estimated to be only 100 m ? The uncertainty in "H" feeds directly into your flux uncertainties, so it is a very important term!

P1166 L21: Descriptions of data plotted in a figure belong in the figure caption, not in the text. In the text, summarize what the data in the graph show and what conclusions are drawn.

P1166 L23-24: Figure 3 does not show that "maritime air masses, initially low in forest hydrocarbons, were advected ...". How can the reader discern that forest hydrocarbons were low in these air masses? What forest hydrocarbons are you talking about?

P1167 L16: Some of the "scatter" in the MeBr vertical profiles was undoubtedly driven the the 0.5 ppt (5%) precision of the measurements and this needs to be stated.

P1167 L22: I think "strong" is overstated here. There is too much scatter in the vertical profiles to make this statement.

P1168 L24: "ambient background" needs support here or "boundary condition" needs to be used instead. This is an important distinction, and unless you can show that the

ACPD

8, S133–S140, 2008

boundary conditions are the same as the ambient background (see comments about Figure 5 above) I would not use "ambient background".

P1169 L9-18: How does "the ML appear to have been influenced by ... air ... advected from a distant burning region"? What exactly identifies distant biomass burning as an influence on the composition of the local ML? This paragraph is very confusing ... discussion of FT air entrained into the ML alongside discussion of boundary layer ventilation and then (L22-23) a final dismissal of entrainment influences. In my opinion, the boundary conditions for ML composition over the rainforest are set at TOL=0 and then the effects of sources, sinks, and transport combine to give you the net observed signals. Boundary layer ventilation may reduce mixing rations in the ML and your flux estimates should incorporate this uncertainty.

P1170: State how you calculated TOL before discussing Figure 5.

P1170 L18: These 4 outliers suggest that not all boundary conditions were "ambient background" (see comment for P1168 L24).

P1171 L13-14 Units on these slopes should be given, pmol mol-1 h-1 (not mol mol-1 h-1 as stated in line 19). Are the mean temperatures and pressures averages for the 0-1400 m range (ML), or averages of the conditions when and where ML samples were collected?

P1172 L22: How might co-eluting peaks affect the GC-ECD results? Which halocarbons might be affected? Could this help to address the CHCl3 flux differences between March 1998 and October 2005?

P1173 L3-4: It should be noted why the Li et al. (1999) MeCl flux is probably so much higher than yours and others - this was a coastal flux study, where chloride ions from sea salt are abundant and fluxes from salt marshes may be strong. I'm not sure it's even relevant to compare your rainforest-wide fluxes to coastal fluxes ?

P1173 L5-7: Please show, in a quantitative way, how "the results presented here are in

ACPD

8, S133–S140, 2008

good agreement with model studies". This statement may need to appear later, after your extrapolation to global rainforests.

P1175 L15: Not necessarily "outweighed", but instead "reduced" to the point that the net flux was too small to measure. Also remember that you are looking at mixing ratio differences and that the 0.5 ppt precision for MeBr measurements hinders your ability to quantify small mixing ratio changes due to the net fluxes.

P1175 L16-19: This sentence needs to be supported or removed. It is a sweeping statement based on a personal communication that, if true, would re-set the entire methyl bromide budget. To make this statement you must provide solid evidence here.

P1175 L22: These statements should be moved to the beginning of the paper.

P1176 L8-12: These global rainforest flux estimates should be put in context of the current net global tropical fluxes of methyl chloride and chloroform. Do your extrapolations make sense in terms of current global tropical fluxes? Are they at the high or low ends of the ranges of global tropical flux estimates?

P1176 L24: How can your global rainforest flux estimates "account for half the missing source postulated by the models" when the WMO 2007 estimates of the gross flux of MeCl from tropical plants and senescent leaves ranges from 850 to almost 11000 Tg yr-1? If the "missing source" from models is now accounted for in the source budget, the source is no longer "missing". The simple perspective is that your estimates are at the low end of the range of net tropical flux estimates, not at the high end, so how can your estimates address a "missing" source?

P1177 L5: You did not make airborne "flux" measurements.

P1177 L15-19: Was the inverse model prediction that you could determine MeBr fluxes by this method? This is not necessarily disagreement, it is the inability of your method and measurements to quantify a net ecosystem flux of MeBr that is statistically different from zero. Does the Warwick paper postulate a gross or net tropical vegetation source

ACPD

8, S133–S140, 2008

of 46 Gg yr-1 ? If gross, you need to account for strong uptake by soils, and possibly by plants, to estimate what the net tropical flux would be. My guess is that this net flux is small, supported by your measurement-based estimate.

Typing/Grammatical/Wording:

P1161 L10 "budget" should be "budgets"

P1161 L16 "until" should be "by"

P1169 L24 "variability" should be "uncertainties"

P1170 L1 "boundary layer air" should be "boundary layer"

P1171 L8 "curve" should be "line"

P1171 L19 "mol mol-1 h-1" should be "pmol mol-1 h-1"

P1172 L19 "Comparing the two studies, which took place in Suriname, one in March 1998 and this one in October 2005" should be "Comparing the March 1998 and October 2005 studies in Suriname,"

P1173 L20 "variation in the CHCl3 flux but no or very little change" should be "difference in CHCl3 fluxes but at most very small differences"

P1177 L24 "is indeed the continuous source of methyl chloride postulated" should be "appears to be a fairly consistent and important methyl chloride source on two different continents"

P1178 L15 "humidity dependence" should be "soil moisture dependence" or "precipitation dependence"

P1178 L19 "top of the knowledge" should be "provide detailed information"

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