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Atmospheric Chemistry and Physics Discussions

Interactive comment on “Isoprene and monoterpene fluxes from Central Amazonian rainforest inferred from tower-based and airborne measurements, and implications on theatmospheric chemistry and the local carbon budget” *by* U. Kuhn et al.

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We like to thank referee #1 for his positive evaluations and helpful comments. Our responses to the specific issues are listed below:

RC #1: “On the pages 650-652 the authors describe the surface layer flux measurement techniques used. However, they don’t mention the effect of the roughness sublayer (e.g. Garratt, 1980) on the surface layer gradient measurements. The possible effect of the roughness should be discussed as it may have a major impact on the fluxes measured above such a rough surface as tropical rainforests are. The effect of roughness sub-layer tends towards lower absolute values of trace gas gradients. Therefore, the observed SLG fluxes, which were higher than REA fluxes (page 658), should be even higher."

AC: According to the referee suggestions we now included this information in the description of the SLG approach: "Applying the SLG approach within the roughness layer of the forest may underestimate the flux rates (e.g. Garratt, 1980). The importance of this effect is dependent on canopy structures and surface characteristics (Simpson et al., 1998) and was not accounted for in the present study. This way the fluxes calculated by SLG are assumed to be a lower bound estimate."

RC #1: "The discussion on the effect of VOC fluxes to the carbon budget (pages 660-663) is somewhat confusing. The estimation of the fraction of the assimilated carbon lost as VOCs does not seem to make much sense if the estimates of the carbon balance vary between strong sink and a weak source. As the magnitude of the VOC emission compared to the carbon balance is an interesting and important topic this discussion should be somewhat reformulated. As the uncertainty and variability of the CO2 exchange seems to provide most of the variation in the comparison, it might be better to start with trying to get the best estimate of CO2 exchange, with range of variation. Also the non-terpenoid VOCs should be mentioned as they may contribute as much as the terpenoids to the carbon balance."

AC: As suggested by Referee #2 this discussion has been edited by way of (i) comparing the numbers of modelled CO2 sink strength of the Amazon with the respective numbers of the VOC fluxes extrapolated for the Amazon forest area (instead of the global rainforest area), both stating absolute numbers (variability and long-term mean) and the relative fractions of carbon re-emitted. Furthermore, the potential source of yet unidentified VOC, and their impact on atmospheric chemistry (OH) is now better described (with cited literature: Dreyfus et al., 2002; Goldstein et al., 2004; and Holzinger et al., 2002). The suggestion of "first trying to get the best estimate of CO2 exchange" for tropical rainforest ecosystem is quite a challenge, and is currently a hot matter of debate, as we tried to highlight in this section. It is beyond the scope of this paper, but references on this debate for the interested readers are given (see also the cited companion paper of Lloyd et al. (2007). However, we give absolute and relative numbers on both the observed local scale and extrapolated to the ecosystem scale.

RC #1:“It is not clear how well the correction for the effect of chemical transformation on the vertical profiles (Page 671, lines 20-22) works for the site with deep and dense canopy. Is the z in the equation (10) height from the ground or from the displacement height? Discussion on how well this correction works would improve the manuscript.”

AC: The z in the equation (10) for the applied chemical corrections is now stated: “As concurrent surface measurements were not available during the flights, the mean ISO, MACR, and MVK mixing ratios measured at the lowermost flight altitudes were used (87 ś 34 m above canopy, see Tab. 3) as starting conditions for the numerical integration (z0=canopy top).” At this lowermost measuring height (˜ 3 times the canopy height) the structure of the canopy should not have an effect (see the newly cited reference Simpson et al. 1998).” The rough concept of our back-of-the-envelope approach does not confer a reasonable tool to investigate the influence of canopy structure and the potential influence of specific turbulent characteristics within the roughness sublayer above the forest. An attempt to check the accuracy of our chemical correction was done by the comparison of corrected isoprene data with the vertical depletion of nonanal. The residual isoprene gradient should be similar to the gradient of nonanal, if nonanal is assumed to not chemically decay in the time scale of CBL convective turnover. The appropriateness of our chemical correction is checked by comparing the contribution of chemistry versus transport/dilution (see chapter 3.3.6).

RC #1: “The title of the paper is quite long. The authors should try to shorten it.”

AC: We actually like the descriptive character of the title and would propose to leave it as is, even though we understand that it is relatively long.

RC #1: “I am not sure if the nomenclature of the spatial scales is correct. Does the MLG technique measure emissions in the regional scale (p. 643, lines 8-9) or in landscape scale?”

AC: Right, now changed to “landscape scale”.

RC #1: “On page 644, lines 21-24 the authors attribute the dominating role of the BVOCs in the lower tropospheric chemistry to their higher reactivity, but do not mention the fact that their emissions are also much higher than those of AVOCs.”

AC: we now state: “The dominating role of biogenic VOCs in the chemistry of the lower troposphere is due to (i) their greater abundance in remote areas and (ii) their high atmospheric reactivity compared to the majority of anthropogenic VOCs (Fuentes et al., 2000).”

RC #1: “On page 647, lines 20-21, the authors give values for LAI and leaf area density of the forest at Cuieiras site. Are these one sided or two sided?

AC: we now state: “a total single sided LAI of Ě”

RC #1: “Page 648, line 18: What exactly were the 2-bed graphitic carbon adsorbents used?”

AC: we now added the details on graphitic carbon used for GC-FID and for GC-MS: GC-FID: “Samples were collected by drawing air through fused silica-lined stainless steel cartridges (89mm length, 5.33mm I.D., Silicosteel, Restek, USA) packed with sequential adsorbent beds of 130 mg Carbograph 1 (90 m2 g-1, Lara s.r.l., Rome, Italy) followed by 130 mg Carbograph 5 (560 m2 g-1).” GC-MS: “VOC were collected using glass cartridges (160mm length, 3mm I.D.) packed with 118 mg Carbopack C (12 m2 g-1, Supelco, Bellefonte, USA), 60 mg Carbograph 1 (90 m2 g-1, Lara s.r.l., Rome, Italy), and 115 mg Carbograph 5 (560 m2 g-1) in sequential beds.”

RC #1: “Page 648, lines 22-24: The sentence, “The detection limit of the method was estimated as the greater of the variability in the blank levels (at the 95% confidence level) or a chromatographic peak three times the noise for each compound...", was not clear to me. What does the variability of the blank level at 95% confidence level mean? Does it mean 1.96 times the standard deviation of the blank values? Also I do not understand what the chromatographic peak three times the noise means. Could the authors elaborate this."

AC: If there is a peak in the respective time window of the blanks, the detection limit was determined by the ability to distinguish a real measurement from the blank peak, expressed as the standard deviation of the blank peak areas at the confidence level of 95% (this is 1.96 times the standard deviation, as the referee suggested). In the absence of a blank peak, one need to be able to distinguish the analyte peak from the noise in the base line. Normally this is considered to be where the analyte peak height is 3 times the standard deviation of the background noise. To clarify, we now state in the text: "The detection limit of the method was estimated as the greater of the variability in the blank levels (at the 95% confidence level, i.e., 1.96 times the standard deviation of all blank values), or a chromatographic peak three times the standard deviation of the background noise in the base line of the chromatograph. Variability in the blank usually determined the detection limit, which was typically 30 ppt for isoprene and 10 ppt for monoterpenes."

RC #1: "Page 649, lines 15-16: I wouldn't call the agreement good when quite often one method gives isoprene concentrations that are at least twice that given by the other method and r2 is only 0.62."

AC: we now rephrased to "reasonable agreement". The exact meaning of this comment is described in detail in the following sentences.

RC #1: "Page 649, line 17 and page 652, line 21: Are the figures in right order? To me it seems that now figure 2 precedes figure 1."

AC: Fig. 1 was already mentioned on page 647.

RC #1: “Page 649, lines 18-20: The length of the sampling into the cartridges could be mentioned here as the differences in the sampling times are mentioned as a possible source of discrepancy between adsorbent and canister samples.”

AC: The sampling interval of cartridge sampling is now mentioned as: “In general a high scatter is expected from the snap-shot sampling characteristic of the canister technique compared to cartridge (15 min, at flow rates of 200 ml min-1) sampling, with short sampling intervals being less representative for mean CBL mixing ratios.”

RC #1: “Page 649, lines 24-28: A more elegant way for estimation of the sizes of the convective eddies in the boundary layer would be the use of spectral analysis. Was there a fast wind sensor mounted on the aircraft and if so, have the authors tried to conduct spectral analysis on e.g. vertical velocities measured in the mixed boundary layer?”

AC: Unfortunately, no fast wind sensor was mounted on the aircraft.

RC #1: “Page 650, lines 1-2: From the sentence “For isoprene, however, they indicated similar trends in vertical profiles, but with a systematic relative underestimation by a factor of 0.55” it is not right away clear what is underestimated, the trend, the absolute concentrations, or both.”

AC: we now clarify by stating: “For isoprene, however, they indicated similar trends in vertical profiles, but with a systematic relative underestimation of the absolute mixing ratios by a factor of 0.55.”

RC #1: “Page 650, line 16: Reference Valentini et al. 1997 is missing from the reference list.”

AC: now added to the reference list.

RC #1: “Page 650, lines 18: What does the “...equal to zero...” mean. The mean wind surely is never exactly zero. What interval around zero is accepted.” and: “Page 650, lines 20-21: What does the sentence “The REA theory was followed when thresholds of w = +-0.65 sigma; were used for conditional sampling” mean?”

AC: we now rephrased this section to: “The VOC-REA system with a reversed geometry (Ciccioli et al., 2003), was installed at a height of 21m above the mean canopy top. Equations used for calculating VOC fluxes are described in detail in Valentini et al. (1997) and Ciccioli et al. (2003). Only those cases were accepted, in which hourly averaged values of the vertical wind (w) were close to zero (between -0.45 and +0.45) and the volume accumulated in the updraft and downdraft traps did not differ more than 10%. From the experience gathered at this site, we have found that the sampling volumes were balanced best if a threshold of +/-0.65 std(w) was used. This means that air was sampled through the updraft (or downdraft) cartridge only if the instantaneous vertical windspeed exceeded this threshold. In the conditions selected, the volume diverted in the two reservoirs ranged between 50 to 60% of the total volume.”

RC #1: “Page 651, lines 5-6: Authors state “...the samplers did not produce any bias within the analytical uncertainty”. Maybe they mean “...the samplers did not produce any bias exceeding the analytical uncertainty”.”

AC: we now rephrased accordingly: “Test samplings with all four inlets mounted at the same height showed that the samplers did not produce any bias exceeding the analytical uncertainty.”

RC #1: “Page 652, lines 6-8: Authors state “According to the footprint analysis of Araujo et al. (2002) the measured daytime fluxes at the K34 tower are representative of a 2-3 km2 area around the tower, although a smaller proportion of the fluxes originates from an area as large as 70-80 km2”. What percentage of the total flux comes from these distances?”

AC: we did a more detailed study on this matter and now state: “According to the footprint analysis of Arajo et al. (2002) the measured daytime fluxes at the K34 tower are representative of a 2-3 km2 area around the tower, although a smaller proportion (ca. 10%) of the fluxes originates from an area beyond 10 km2 around the tower.”

RC #1: “Page 654, line 14: Could the authors specify what exactly they mean by discontinuity and inflection.”

AC: A characteristic of the CBL is the presence of small or medium scale mixing processes (turbulence) providing for rather homogeneous properties throughout the CBL, but large changes of properties occurring at the CBL top. The altitude where the maximum of the variance of trace substance concentration occurs is often identified as the CBL height (Stull, 1988). To clarify, we now state in the text: “The height of the CBL is defined as the height where the potential temperature and other scalar profiles have a maximum of the variance (Stull, 1988). In most cases zi could be estimated as the lowest altitude at which the potential temperature profile showed a persistent change from well mixed to subadiabatic conditions. Where this was not clearly indicated, the profiles of H2O, CO2, and other measured trace constituents like CO, ozone, and aerosols were taken into account.”

RC #1: “Page 655, lines5-15: Are the VOC emissions in the model calculated using Guenthertype parameterizations?”

AC: Yes, as we now state: “VOC emissions were calculated according to Guenther et al. (1995).”

RC #1: “Page 656, line 20-21: Maybe it should be mentioned that the site can be expected to be representative of undisturbed rainforest during easterly winds.”

AC: we now state accordingly: “With vast expanses of pristine forest situated to the east of the K34 tower, this site can be expected to be representative of an undisturbed remote rainforest ecosystem during easterly winds.”

RC #1: “Page 657, lines 6-7: How low the benzene and toluene mixing ratios were?”

AC: we now state: “Toluene and benzene mixing ratios were relatively low (≤ 0.1 ppb) and did not show distinct vertical profiles, indicative of the absence of human activities or other significant air pollution sources at this remote forest site.” Moreover, the respective REA fluxes are now given in section flux 3.2.1.: “For anthropogenic VOC mainly deposition was observed. In particular average daily fluxes of -0.21, -0.02 and less than -0.01 mg C m-2 h-1 were measured for benzene, toluene and CCl4 during this campaign. These values are similar to those reported previously for the same site (Andreae et al., 2002).”

RC #1: “Page 659: lines 4-6: “The diel course of mean modelled fluxes of all measurement days shows good agreement with observations, and revealed a range in between those calculated by REA and SLG”. The wording of this sentence seems odd. What did the modelled fluxes reveal?”

AC: we now rephrased to: “The diel course of mean modelled fluxes of all measurement days were in a range between those calculated by REA and SLG (Fig. 5, middle panel), and hence showed good agreement with observations.”

RC #1: “Page 666, lines 5-9: This section is confusing. Could it be rephrased to make it more understandable?”

AC: In accordance with the comments of referee #2 this section is now rephrased to: “Close to the canopy top the production of MVK and MACR is supposed to be largest (due to high isoprene mixing ratios) and the influence of further oxidation is small. Also the mean velocity shear is largest in this surface layer, with the largest turbulence kinetic energy; hence here the smallest chemical modification occurs. This is different for the airborne data within the CBL, where the chemical production of MVK and MACR is smaller (due to lower isoprene mixing ratios) and the compounds are subject to chemical degradation for longer time periods.” Further details of this issue were given on page 664 line 26 to page 665 line 4.

RC #1: “Page 673, lines 8-10: “Presuming that nonanal is biogenic and can be considered as a conserved scalar within the time scales of CBL convective turnover, its atmospheric depletion is largely driven by turbulent mixing”. I assume that the authors mean that its surface layer depletion is mainly driven by turbulent mixing.”

AC: this section is now rephrased to: "Ě its depletion with height is largely driven by turbulent mixing."

RC #1: "Page 675, line 19: Expression "principal difficulty" sounds strange to me."

AC: now replaced by: "Ě ultimately generating conceptual and practical difficulties".

RC #1: "Page 676, line 5: Do the authors mean chemistry corrected gradient by "effective gradient"?

AC: now more precisely described by: "The photochemical oxidation of VOCs within the CBL contributed considerably to the shape of their vertical profiles, and neglecting chemical destruction of VOCs was shown to cause a systematic overestimate of the effective gradients applied to calculate VOC fluxes."

RC #1: "References: The references are incomplete. In many cases page numbers or doi is missing, making it hard for the reader to find the cited papers."

AC: now completed where applicable.

RC #1: "Table 1: In the study by Rinne et al. (2002) isoprene flux was measured by eddy covariance (using FIS), and a-pinene by disjunct true eddy accumulation, not disjunct relaxed eddy accumulation."

AC: Table 1 now changed accordingly.

RC #1: "Figure 6: Would it be possible to show also errorbars for the measured fluxes."

AC: the error bars are now given in Fig. 6.

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