

Interactive comment on “Impact of Manaus City on the Amazon Green Ocean atmosphere: ozone production, precursor sensitivity and aerosol load” by U. Kuhn et al.

U. Kuhn et al.

uwe.kuhn@art.admin.ch

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Final Author Comments (AC)

Anonymous referee #1 comments (RC C4573: 'Manaus Ozone Formation', Anonymous Referee #1, 29 Jun 2010):

“The paper should be published. The concept of a green ocean is illuminating and the idea of following ozone evolution in this environment with a view toward development policy highly commends this paper for ACP. The sampling was intelligently performed and the authors are to be congratulated for carrying out synthesis of the information. Also of interest are comparisons made between 1985, when some of the first Amazon

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“green ocean” atmospheric composition flights were made, and 2001. However, the paper is too long and diffuse in some places. I suggest removing selected figures and putting aerosol material in a separate paper.”

Anonymous referee #2 comments (RC C4673: 'review', Anonymous Referee #2, 01 Jul 2010):

RC#2: The manuscript Impact of Manaus City on the Amazon Green Ocean atmosphere: ozone production, precursor sensitivity and aerosol load by U. Kuhn and co-workers is an excellent written and structured paper. I also want to point out the fantastic job the authors did in the review of the literature; the manuscript presents on many topics discussed a comprehensive overview what has been done. One critical point as has already mentioned by the other referee is the length of the paper, which is on the edge and I also recommend shortening it. Below are some advices to cut the length of the manuscript which could be easily worked out and in agreement with referee 1. After considering the small comments from both referees I would strongly suggest to publish this paper in ACP.

Final Author comment (AC): We like to thank both referees for their positive evaluations and helpful comments. Both referees stress the length of the paper. We do agree with the referees that “the length of the paper is on the edge (RC#2)” for a publication in an online journal like ACP. One way to easily accomplish a substantial reduction of the paper length would indeed be to cut the aerosol issue in the introduction/results/discussion sections and solely focus on trace gases. However, we would like to take this opportunity to emphasise our opinion that these two issues (trace gases and aerosols) are tightly linked together. Times are now approaching where trace gas atmospheric chemistry issues should not be assessed without consideration of the particle phase chemistry (e.g., heterogenic reactions) and vice versa. We understand this paper as an overview of what has been achieved by the LBA-CLAIRE airborne campaign, with emphasis on both the temporal/spatial development of trace gas chemistry (ozone production) within the Manaus City plume, and the particle phase. Both go in

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concert and should not be separated in two different papers. Both issues are part of the same story, and separation would be at the reader's expense of losing the one or the other information contributing to a comprehensive picture of the influence of the Manaus City on Green Ocean air. As cited in the paper (conclusion section): "As the formation of photooxidants and aerosols is tightly linked together through atmospheric chemical processes, respective emission reduction strategies must be evaluated together, as a strategy that is optimal for aerosols may interfere with an ozone reduction strategy, and vice versa (Meng et al., 1997; Neftel et al., 2002). ... Specifically the interactions and feedbacks between natural and anthropogenic sources of aerosol precursors are important for the aerosol loading and need to be investigated based on a detailed physical and chemical characterization and quantification in future experiments."

We do have to admit, that - for the time being - we are not in the position to resolve these complex linkage/dependencies, but we think that the apparent existence of this linkage is an effectual condition to assert the continuance of the aerosol chapters within the paper.

Furthermore, separation of the paper into two separate papers would increase the net number of pages required, as redundant introductions, method sections, reference lists, etc. would be required. It is also quite clear that the aerosol paper could not be understood without the information in the trace gas paper, including the presentation of the plume dispersal, etc., which would force the reader to work through two separate, but mutually dependent papers. We had given this idea quite some thought before deciding on submitting just one, admittedly large, manuscript, but ended up with the conclusion that the reader would be better served with one longer paper.

Minor corrections:

RC #1: PAGE 3- Line 25 - references on OH - Logan, JA; PRATHER MJ; WOFSY SC; MCELROY MB. TROPOSPHERIC CHEMISTRY - A GLOBAL PERSPECTIVE ... Look

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up in JGR also, Thompson, AM, Science, 1992: both

AC: now included

RC #1: PAGE 3 – Line 29 - The word "being" is not needed

AC: now omitted

RC #2: Chapter 3.7: I do not see any need to repeat all the theory of the model in the beginning of this chapter as all this was already discussed before and would start direct on page 13128 line 24:

AC: We find this a good place to give a short extract on VOC and NO_x sensitivities, with respect to the title of the paper ("precursor sensitivity"); however this paragraph has now been shortened, as:

Atmospheric ozone production over an urban centre involves different stages, from being VOC-sensitive near the source(s) to being NO_x-sensitive further downwind; i.e., P(O₃) being either more sensitive to a small fractional change in VOC mixing ratios or to a small fractional change in NO_x mixing ratios (e.g., 2000; Sillman, 1999). Fresh emissions of NO_x are primarily (>90%) emitted as NO, leading to titration (degradation) of background ozone in the vicinity of the source. In the course of plume dilution a photostationary state will be reached between NO, NO₂ and O₃ within minutes. High mixing ratios of NO₂ (NO_x-saturated) in the fresh plume will act as (OH) radical scavenger, suppressing VOC oxidation. Consequently, the production of nitric acid (HNO₃) is much higher than the production of organic peroxides, and net ozone production is linked to the consumption of VOC. An increase in VOC emissions then leads to an increase in peroxy radicals that convert NO to NO₂, ultimately causing an increase in O₃ (VOC-sensitive ozone production). In the NO_x-saturated stage, an increase of NO_x emissions would scavenge even more radicals, diminishing the oxidizing capacity and hence net O₃ production of the air parcel. During chemical aging of the plume further downwind, NO_x levels decrease due to dilution, deposition and the chemical production

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of HNO₃ and/or PAN, ultimately reaching a threshold where availability of NO₂ poses a limitation for ozone production (NO_x-sensitive). OH radicals then predominantly react with VOC instead of NO_x, generating organic peroxides. As a consequence the production of HNO₃ is reduced and a higher share of NO_x may participate in the catalytic ozone production cycle, with organic peroxides being the major contributor to recycle NO₂ (from NO) for ozone production. In this last stage, variations in VOC have little effects on ozone production and peroxy radicals are removed at relatively low rates mainly via recombination reactions.

RC #2: Page 13111 line 12: rations -> ratios

AC: now corrected

RC #2: Page 13120 line 26: ... in the boundary layer of above tropical forest ... -> remove of

AC: now removed

RC #2: Figure 8: CCN₀₆ there is one space should be removed

AC: now removed

RC #2: Figures 14-19: It would be easier for the reader if the measured values would be included in the model plots so it is not always necessary to check what was the concentration of the selected parameter when viewing the model outcomes.

AC: Measured and modelled values change with time and three-dimensional space. We find adding additional data in Fig. 14-16 too complex to comprehend. The idea of the model output diagrams is rather to show that the model predicts trace gas concentration in similar ranges to what was observed. Here the reader is reliant on the text where this is already stated:

for Fig 14: CO and NO_x ... appear to be at the lower range of the corresponding Manaus plume average observations (Fig. 8).

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for Fig. 15: ozone ... is in good agreement with observed O₃ mixing ratios of ~50 ppb at about 400 m altitude 10 km downwind of Manaus.

for Fig. 16: power plant NO_x mixing ratio ... representative of the concentration range within the plume transects observed at this distance (see Fig. 8).

for Fig. 17: strong titration of ozone ... is well reflecting the observations shown in Fig. 8.

for Fig. 18 and Fig. 19: the O₃ process tendency and the OH radical concentration was not measured directly, so no direct comparison ...

RC #2: Page 13108 line 22: The authors mentioned that background aerosols are elevated relative to truly unpolluted pristine rainforest values and conclude that because this measurements were performed downwind of Manaus region where true background values could not be reached. On the other side they mention that CO values are at the lower end of CO concentrations in the CBL observed during the campaign, which indicates that this flight fell into a relatively unpolluted period. I cannot understand why we should get more dilution of aerosols in the plume and outside compared to CO and this needs to be better explained as it is done on page 13106 at line 1-4. This stands also in conflict with the statement page 13114 line 24: all plume components are expected to be equally affected by plume dispersions in the BL Also by viewing figure 5 the values at the edge seem to be much lower (green color) as shown in figure 3.

AC: now specified more clearly:

Aerosol concentrations during LBA-CLAIRE-2001 were somewhat elevated relative to truly unpolluted pristine rainforest values, with mean values of aerosol number concentrations (CN) within the CBL of 700-1700 cm⁻³ and CCN_{0.6} concentrations of 400-1200 cm⁻³, both decreasing with altitude (Fig. 3, Table 1). The cleanest conditions during LBA-CLAIRE-2001 were reached after the aircraft campaign, during 23-25 July, when

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the average CN concentrations at Balbina were $513 \pm 160 \text{ cm}^{-3}$. Values of 400-500 particles cm^{-3} are typical of unpolluted Amazonia in the absence of extensive precipitation (Roberts et al., 2001b; Andreae et al., 2004; Andreae, 2009; Martin et al., 2009, 2010; Pöschl et al., 2010). In general, the background aerosol concentrations obtained on the aircraft were in good agreement with simultaneous measurements made at a ground-based site, located at Balbina, some 125 km NE of Manaus (Table 1). During some flights the background CN concentrations measured on the aircraft were slightly higher than those measured at Balbina, which may have been due to the flights being located generally downwind of the Manaus region, where minor amounts of pollutants may have been present. Because of the very high aerosol enhancement in the Manaus plume relative to that of CO (average $\Delta\text{CN}/\Delta\text{CO} = 340 \pm 230 \text{ cm}^{-3} \text{ ppb}^{-1}$, see Section 3.6) a CN enhancement of about 200 cm^{-3} , as was observed on #Flight 18, would correspond to a CO enhancement of less than 1 ppb, which could not be distinguished from the regional background.

Interactive comment on Atmos. Chem. Phys. Discuss., 10, 13091, 2010.