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Atmospheric Chemistry and Physics Discussions

Interactive comment on "A Lagrangian analysis of the impact of transport and transformation on the ozone stratification observed in the free troposphere during the ESCOMPTE campaign" *by* A. Colette et al.

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Abstract

This letter answers the comments of two anonymous Referees. Modifications in the text of the manuscript originally submitted are made accordingly. We believe that these changes will significantly improve the quality of the paper and therefore we wish to thanks the Referees for their constructive comments.

The present document follows the outline of the Comments of the Referees, by addressing each point separately and referring to the modifications of the original text. The major change to the original manuscript follow the suggestion of Referee #2 in its point 2 to re-organized significantly sections 3.3.2 and 3.3.3 of the paper.

So that Sect. 3.3.2 is now "Uncertainties of the chemical initialization" and Sect. 3.3.3 is "Results of the Lagrangian photochemical simulation".

1 Referee #1 General Comments:

1.1. In its general comments, Referee #1 regrets the restriction of the present study to the analysis of ozone LIDAR observations whereas physical and chemical characterization of the lower troposphere in the area during the ESCOMPTE campaign included several other instruments.

The purpose of this paper is to investigate the influence of transport processes on the spatial and temporal variability of free tropospheric ozone. Therefore, we chose to focus on tropospheric ozone lidar measurements that provide with resolution vertical and temporal observations with a complete temporal coverage of Intensive Observing Periods. As mentioned by the Referee, airborne and balloon borne ozone observations were performed during the ESCOMPTE campaign. However, we chose not to include these data in the present study, considering that most of the information on spatial and temporal variability of ozone is captured by the lidars. For more details on these complementary observations, the reader is referred in section 2.4 "Ozone profiling" to Ancellet and Ravetta (2005) who provide a thoughtful comparative analysis of all kind of ozone data. As far as CO and aerosol measurements are concerned, we agree that a complementary discussion would improve the paper (see next point).

2 Referee #1 Majors Comments:

2.1. The Referee #1 suggested including a discussion of carbon monoxide and aerosols measurements to reinforce the discrimination of stratospheric and polluted

ACPD
6, S1414–S1423, 2006

air masses.

The authors decided to implement this suggestion in the paper considering that:

- Aerosol measurements performed by the ALTO lidar are presented in Ancellet and Ravetta (2005). For ozone-rich air masses selected in the present study, the aerosol backscattering ratio is of the order of 1.2 (1 being the reference for no aerosols). This is consistent with a non-stratospheric origin.

- Carbon monoxide measurements were performed on board the Dornier aircraft (Said et al., 2005). For the 24th of June, two horizontal legs at 900m and 2800m asl were performed in the vicinity of the ALTO lidar (not shown). At 900m, carbon monoxide variability is high, with very clean air masses ([CO]=100ppbv, probably maritime air masses) and small pollution plumes ([CO]=200ppbv) on the Easternmost section of the flight. On the contrary, the 2800m altitude leg - corresponding to the ozone layers discussed in the paper - shows a more homogeneous CO field with CO content of the order of 150ppbv. This is consistent with aged polluted air masses, and discriminates unambiguously any stratospheric origin. This discussion has been added in the paper under section 2.2 "Selection of the time frame" as it complements in an interesting way the evidences used in the selection of air masses that can illustrated mesoscale coupling between the planetary boundary layer (PBL) and the free troposphere (FT).

2.2. Considering that airborne NOx measurements used in the present paper were not published before in the open literature, the Referee #1 requested to add it in the paper.

The instrument is described in Marion et al. (2001) and the experimental setup is given in Coll et al. (2005). After discussion with the PI of the MONA instrument (P. Perros), it appeared that these data were not published explicitly before. Consequently, we decided to include the average NOx profile for the three flights of June 23rd, 24th, and 25th as well as minimum and maximum values in section 3.3.3 "Results of the Lagrangian photochemical simulation".

ACPD

6, S1414–S1423, 2006

3 Referee #1 Minors Comments:

3.1. On the concern of Referee #1 regarding FLEXPART's capability to reproduce venting processes from the PBL.

As described in Stohl et al. (2005), the FLEXPART model accounts for subgrid scale processes such as orographic venting and convective activity. However, its efficiency at detecting air masses extracted from the PBL through a wide range of dynamical processes depends on the accuracy of this parameterization which might be limited for highly complex terrain. Consequently, as suggested by the Referee, we preferred a non-hydrostatic mesoscale model which gives a better representation of venting processes by small scale thermal gradients and above complex orography. Section 2.2 "Selection of the time frame" has been slightly modified to account for this discussion.

3.2. Referee #1 requested a clarification of the statement regarding the similar ozone content of air masses coming from very widespread geographical locations.

The purpose of this statement was just to warn the reader that a single tracer (ozone) may not necessarily reflect the whole variability of air masses. The sentence was slightly rewritten in Sect. 3.1.2 "Mesoscale trajectories".

3.3. Referee #1 suggested adding an additional plot of O3 variation to illustrate ozone production.

This information is included in Table 1 as production rates of each cluster and a reference to this table was added in Sect 3.3.3 "Results of the Lagrangian photochemical simulation". Two entries were added in this table to give the average altitude and time of arrival of the clusters in order to facilitate cross reading of Fig. 4, 5 and 6 of the paper.

3.4. Referee #1 requested additional information regarding the comparison between CHIMERE outputs and EMEP surface NO2 measurement in Spain.

ACPD
6, S1414–S1423, 2006

The standard deviations of modeled and measured NO2 have been added in Sect. 3.3.2 "Uncertainties of the chemical initialization" in the comparison between observed and modeled NO2 levels. Regarding the averaging process, in this section we refer to temporal averages at the exact location of the stations. The records of Spanish surface stations are averaged during the whole time period and modeled NO2 in CHIMERE outputs are averaged temporally at the exact geographical and vertical location of the stations.

3.5. On the relevance of the two NOx scenarios described in the study.

The analysis of the reference run showed a pronounced underestimation of simulated NOx at the end of the trajectories. And the verification of NO2 levels at the initialization of the trajectories suggested an underestimation in the CHIMERE model. Altogether these features justified the need for a sensitivity analysis to the less well constrained parameter: NOx. But the range of sensitivity explored had to remain within reasonable limits, i.e. those prescribed by the comparison with EMEP measurements. Even if, as noted by Referee #1, none of the scenarios is successful at reproducing observed NOx levels at the end of the trajectories, the enhanced NOx run is close to the observations. On the processes responsible for an underestimation of NOx levels at the initialization of the trajectories, the mechanism highlighted by Parrish et al. (2004) could occur. Parrish et al. mention that NOx are relatively efficiently vented toward the free troposphere through deep convective events, but that shallow venting toward the entrainment layer is not well resolved by global CTMs. And we can note that underestimation of NO2 levels compared to EMEP measurements is less pronounced at low altitude stations than for stations located above 800m asl. This observation corroborates the hypothesis of an inappropriate representation of shallow venting of trace gases in the PBL in the CHIMERE model. This discussion has been added in Sect. 3.3.2 "Uncertainties of the chemical initialization".

3.6. Referee #1 asked further explanation of the decrease in ozone photochemical production for cluster 23 with increasing NOx.

ACPD

6, S1414–S1423, 2006

As shown in Fig. 5b of the paper, the initial NOx level in this cluster is very high. By increasing its initial NOx content, one shall switch photochemical regime to NOx saturated regime as described in Sillman (1990). Note also that cluster 23 is not the only group of trajectories with high initial NOx content. But its little significance (with only 5 trajectories in the cluster, see Table 1 of the paper) allows identifying this change in regime, whereas it is averaged out in larger clusters. This discussion was added in Sect. 3.5 "Ozone production efficiency".

3.7. On the significance of ozone comparisons:

As requested by the Referee, we added standard deviations in the section 3.5 "Ozone production efficiency". In the text, the statistical significance of the comparison is checked with a Student test at the 95% confidence level rather than comparisons of averages and standard deviations.

4 Referee #2 Comments

4.1. On the choice of the TKE criterion for the selection of air masses coming from the PBL

The threshold we used in the present paper was suggested by the authors of the semi-lagrangian air mass tracking routine in the MesoNH model, as described in Gheusi et al. (2005). The reference was added in the text in Sect. 3.1.2 "Mesoscale trajectories".

4.2. The Referee #2 requested to re-organize sections 3.3.2 and 3.3.3.

The Authors agree that these sections could be improved and the text was significantly modified to account for this request.

4.3. On the comment on Referee #2 regarding trajectories where ozone is degraded during the transport.

ACPD
6, S1414–S1423, 2006

EGU

Even if in the reference run we do find 31% of the air parcels with a lower ozone content at the arrival compared to initial concentrations, we must temperate this value. Indeed most of the production rates are actually very close to zero and ozone loss is lower than -4.6ppbv for only 5% of the air parcels. Trajectories belonging to this lower extreme have higher ozone (75.2ppbv) and lower NOx (0.68ppbv) content at the initialization of the trajectories compared to the global average (O3=68.6ppbv, NOx=1.35ppbv), which suggest that ozone was produced in the PBL before the export to the FT. But in the absence of mixing, this ozone decrease must be the result of a specific chemical mechanism. By looking at Table 1 of the paper, one shall notice that the clusters with lowest ozone production rates have longer residence time in the FT. Also most of these trajectories were transported during longer periods of nighttime than the average. They could thus have been exposed NOx saturated regime not balanced by daytime photochemical production of ozone. However, it is difficult to draw robust conclusions on the respective impact of the fraction of nighttime transport and initial chemical composition because of the complex interplay between these factors. Section 3.3.3 "Results of the Lagrangian photochemical simulation was modified to account for this discussion".

4.4. Referee #2 asked further clarification for the choice of climatological CHIMERE fields in the mixing scenarios.

Mixing with actual 3D fields prescribed by the CTM would be relevant if one expected that the Lagrangian boxes were transported in the vicinity of air masses that (1) had physico-chemical characteristics significantly different from climatological values and (2) were not captured by the MesoNH model. But in our choice to test the mixing with a climatological field, we considered that (1) dynamical models of CHIMERE and MesoNH differ, (2) in the present study the best resolution is that of MesoNH and (3) semi-lagrangian advection in MesoNH is expected to be more reliable. Consequently we have no reason to imagine that the Lagrangian air masses (following MesoNH trajectories) have encountered an air mass with different chemical characteristics that were successfully reproduced by the CTM and not simulated in the MesoNH simula-

ACPD
6, S1414–S1423, 2006

tion. The text of section 3.4.1 "Methodology" has been slightly modified to make this clearer.

4.5. On the concern of Referee #2 on the sensitivity of the photochemical box simulations to parameters not tested in the present study such as water vapor and photolysis rates.

As described, e.g., in Kleinman et al. (1997), ozone photochemical production is constrained by (1) the availability of NO, (2) loss of hydroxyl radicals through recombination with NO2, and (3) production of HOx (=OH+HO2+RO2). Consequently, for low NOx concentrations such as in the study of Reeves et al. (2002), water vapor mixing ratio can play an important role in ozone photochemical production. However, in our study, NOx concentrations are much higher than in the oceanic free troposphere (as in the Reeves et al. study), consequently, P(O3) will be primarily driven by NOx and VOC whose variability is very high in the present study.

Still, the authors agree with the reviewer that ozone photochemical production could be modulated by the variability of water vapor mixing ratio. But our aim was not to conduct a sensitivity study of P(O3) to all the possible parameters involved. The purpose of the present paper was to identify the major mechanism responsible for the observed ozone variability during this regional pollution event. Consequently, we have limited our analysis of P(O3) to the testing of the less well defined parameter: NOx concentrations.

On the contrary, water vapor is well constrained as the mesoscale model proved to be successful at modeling water vapor above the measurement site (NB: in the Lagrangian chemical model, water vapor, temperature, pressure, etc are prescribed by the mesoscale dynamical model). During the campaign, 4 daily soundings were conducted in the ESCOMPTE area. These soundings were not assimilated in the analyses used to drive the mesoscale model, but the agreement between model and observations shows that most of the variability is well reproduced by MesoNH (not shown). As far as photolysis rates are concerned, we also obtain a good agreement between the

ACPD
6, S1414–S1423, 2006

EGU

CiTTyCAT model and measurements on board the Dornier aircraft in the ESCOMPTE region. Observed JNO2 exhibited very little sensitivity to surface heterogeneity, and during this period, the area was largely cloud-free. Consequently, JNO2 depended mostly on the time of the day and altitude, and was thus correctly reproduced by the Lagrangian box model in the ESCOMPTE region. Unfortunately, we can not check modeled JNO2 during the transport against observations. But METEOSAT images showed that the air parcels were transported in a cloud-free atmosphere, except at the beginning of the transport, where shallow cumulus cloud developed occasionally in relation with PBL venting. Section 3.3.2 "Uncertainties of the chemical initialization" has been significantly completed to account for this discussion.

4.6. On the comparison between P(O3) estimates according to the hybrid-Lagrangian approach and global and regional CTMs

The reference to the global model of Liang et al. (1998) was given to offer to the reader a point of comparison, rather than to compare the efficiency of one approach or the other. This study was chosen because it proposes a quantification of direct export of ozone and transformation in the free troposphere, whereas it is not so straightforward to evaluate from CTMs outputs. We agree with the referee that evaluation of CHIMERE outputs using these observations would have been interesting, but it is out of the scope of the present paper as explained below.

i. Referee #2 asked whether the CHIMERE model was capable to reproduce the observed variability in ozone in the FT during the IOP. Yes, to some extent. The large ozone rich layer was successfully modeled by the CTM, but average ozone was slightly over estimated (75.3$\pm$3.4ppbv compared by 72.9$\pm$7.3 according to the ALTO lidar). Also, because of the inherent diffusive character of the CHIMERE model at the resolution used in the present study, the variability of ozone is much lower. But the main motivation to develop an alternative approach, was to investigate the mechanism responsible for the ozone variability, while the CTM only gives an instantaneous picture of the ozone field, and is not appropriate to track the dynamical and photochemical

ACPD
6, S1414–S1423, 2006

EGU

history of air masses.

ii. The Referee asked if the CHIMERE model agreed with the estimates of P(O3).

As mentioned in the previous point, final ozone concentrations in the ESCOMPTE area modeled by the CHIMERE model are relatively similar to the observations. And the initialization of the Eulerian and Lagrangian photochemical models are identical. Consequently, we can conclude that P(O3) given by CiTTyCAT and CHIMERE should be comparable. However, with the Eulerian approach, we can not quantify directly P(O3) during the transport of an air parcel.

iii. The Referee #2 wondered whether the CHIMERE model suggested similar processes. Again, the answer to this question follows the same lines as the previous point. With a 3D CTM, it is difficult to perform an objective assessment of the processes involved. The widely used methodology consists in shutting down one or the other source to conclude on the processes involved. But our approach offers a direct insight into the respective impact of transport and photochemical transformation.

These points have been added in the text under sections 3.3.3 "Results of the Lagrangian photochemical simulation" and 3.5 "Ozone production efficiency".

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