Response to comments from referee #2 - A Lagrangian view of ozone production tendency in North American outflow in summers 2009 and 2010
MS Number: acp-2013-350

Summary:
This paper presents an evaluation of ozone production and loss in air masses lofted from the North American boundary layer, transported across the North Atlantic and sampled at the Pico Mountain Observatory (PMO) in the Azores. This paper addresses an important topic: an improved understanding of the ozone budget in the more remote regions of the northern midlatitudes. PMO is very well positioned to provide measurements to elucidate this aspect of tropospheric chemistry. However, I do not believe that this paper in its present state is near ready for publication. In my judgment there are clear indications of serious problems in the analysis presented. It is not clear to me if these problems can be easily repaired, or if a different analysis approach is required. The paper should be rejected with encouragement to resubmit a manuscript with improved analysis. There are two major concerns that require attention, as detailed below.

We thank the referee for this review, which provides valuable insights and comprehensive discussion about the results and conclusions of the manuscript. The referee has two major concerns about the manuscript. First, the referee suspects some results did not show a strict Lagrangian view and questioned the modeling approach used in the manuscript. With regards to this concern, we added reasons why a perfect Lagrangian view cannot be achieved with this approach, and decided to change the title from “A Lagrangian view…” to “A semi-Lagrangian view…”. We also carefully re-examined the model settings and calculation codes. We found an error in the folding calculation which was responsible for the unexpected NO_y increase in the results for the 2010 Event. The second concern from the referee is in regards to the validity of the ozone-CO correlation analysis in the manuscript. In this response and the revised manuscript, we explained that different sources of background air did not likely affect the ozone-CO correlation analysis for the specific cases we chose. In addition, we also incorporated more data resources to support our findings. As a result of the revisions in response to the referee comments, we hope that the manuscript is publishable in this journal.

Important Concerns:
1) As the title of the paper makes clear, the authors apply a Lagrangian approach in their analysis of pollution plumes during transport. Hence, I expect the concentrations of species in the plume to evolve in a physically reasonable manner. However that is not the case for the concentration changes illustrated for the two plumes examined in detail (Fig. 6). Specific concerns include:

A Lagrangian view of chemical evolution in pollution plumes was achieved by combining a global chemical transport model (GEOS-Chem) and a particle dispersion model (FLEXPART). In the manuscript, chemistry was calculated in GEOS-Chem, and the chemical evolution of the plume was then determined by sub-sampling GEOS-Chem with FLEXPART retroplumes. If the transport between the two models were perfectly identical, then FLEXPART would consistently sample the same part of the GEOS-Chem plume at every time step. A perfect Lagrangian view would be obtained in this way and chemicals would be conserved in the folded results. The referee suggests that some species did not behave realistically, and that therefore the method must be defective. To address the issues related to Lagrangian transport, we have expanded on the discussion of Lagrangian transport in the revised manuscript by more fully describing two technical difficulties that prevent the method from providing perfect Lagrangian simulations. We have also carefully re-examined the program code for doing the folding calculation and found an error that was responsible for the unexpected NO_y increase in the 2010 Event. A general explanation is given in the next two paragraphs. Responses to each issue raised in the referee bulleted points are provided later.

The greatest difficulty with this method is the fundamental difference in transport driven by the different meteorological fields employed by GEOS-Chem and FLEXPART. To address this issue, in Sect. 3.3.2, we examined the relative agreement in transport between FLEXPART and GEOS-Chem for the events. The test verified the occurrence of Event 2 and 6 in both models and revealed agreement of transport in the simulations. However, as discussed in Sect. 3.1 in the work of *Owen and Honrath* (2009) in which the method was first published, some degree of disagreement should be expected between the transport processes in different modes of two models. Additionally, random components and different approaches to transport mechanics (e.g., turbulence parameterization and convection mechanics) can negatively affect transport agreement between the two models such that even when the major wind components result in similar transport, the FLEXPART retroplume could move around in the GEOS-Chem fields and sample slightly different parts of the GEOS-Chem plume, as shown in Figs. 7 and 8. For example, in the first column of Fig. 7, the retroplume was predominantly at 3.3-4.1 km at 2.8 days upwind of PMO after the retroplume had coalesced (Panel (b)), while the plume in GEOS-Chem was distributed over a broader vertical range from 2.0-4.2 km as shown by the CO profile. As a result, the retroplume sampled in the higher portion of the GEOS-Chem CO plume at this time. One day later (in Panel (c)), the retroplume moved lower to 2.8-3.8 km, while the plume in GEOS-Chem distributed from 2.0-5.0 km. Thus, the retroplume sampled a different part of the pollution plume in GEOS-Chem compared to one day earlier. The discrepancy does not have a significant impact on the Lagrangian view of relatively stable species such as CO and ozone because the retroplume still sampled at the altitude where these species mostly concentrated. However, this discrepancy could significantly affect the results of species such as NO_x and PAN, which might concentrate at different altitudes within the broader GEOS-Chem plume due to the sensitivity of these species to ambient conditions (e.g., wet removal or thermal decomposition). For example, from Panel (b) to Panel (d), due to the slight movement of the retroplume, the peak CO mixing ratio sampled by the retroplume was approximately 85 to 95 ppbv, whereas the peak NO_x sampled by the retroplume increased significantly from 0.03 ppbv to 0.06 ppbv. A more detailed explanation and the manuscript revisions are provided under the second bullet within this major comment.

The second major difficulty in achieving a perfect Lagrangian sampling with this method is driven by the numerical diffusion inherent in an Eulerian model. This artificial diffusion may lead to extra dilution of the plume, which can also cause a non-perfect Lagrangian view (as discussed on page 15166, line 15 in the manuscript). As a result of numerical diffusion, chemicals are automatically diluted in grid cells at each time step such that a concentrated plume can be displaced in the next step (*Owen and Honrath*, 2009) and is not sampled correctly by FLEXPART retroplumes. For example, a concentration gradient of a chemical in GEOS-Chem may cause such an artifact, as discussed on pg. 15166, line 22-28 of the manuscript. When intensive vertical movements of the atmosphere occur, this effect can cause unexpected air mass exchange between the plume and the surrounding air, which may disrupt the consistency of the folding process. As stated on page 15166 line 27 in the manuscript,

> “This artifact caused by numerical diffusion in GEOS-Chem can be minimized by running simulations at a higher resolution.”

These artifacts were known at the outset of this work, are the primary reason we carefully examined the events for transport agreement and also refer to the method as a “semi-Lagrangian approach” in the manuscript. To make it clearer to the reader that there are limits in this Lagrangian approach, on pg. 15149, line 25 we added,

> “This semi-Lagrangian approach uses backward FLEXPART simulation results to sample air masses in an Eulerian GEOS-Chem field. There are three features of this method that prevent it from providing a perfect Lagrangian view. The fundamental aspect is the difference in meteorology fields driving the two models. GEOS-Chem uses the GEOS meteorology fields while FLEXPART is driven by GFS fields. Although both GEOS and GFS are considered to be valid simulations of meteorology, some degree of discrepancy is expected between them. The second feature is the result of random components in the models, including turbulence and convection mechanics, which were noted when the method was first published (*Owen and Honrath*, 2009). Finally, inherent numerical diffusion in GEOS-Chem can lead to extra dilution of pollution plumes. This last issue can be reduced by using higher resolution simulations but cannot be entirely avoided. Given the large scale of the particular events that met our criteria (10 °lat x 10 ° lon), the folded results are still able to adequately reflect a Lagrangain view of chemical processing. However, some chemical species in the plume may deviate from mass conservation and the magnitude of deviation may vary for differing conditions, e.g., transport types or properties of species. In regards to the affected results, specific issues are discussed as they arise.”

In addition, because the current title of the manuscript may be misleading, we decided to change “A Lagrangian view…” to “A semi-Lagrangian view…”.

- In the absence of loss due to precipitation scavenging or input from lightning, NO_y should be conserved in a Lagrangian plume, although its concentration may decrease due to dilution by air from outside the plume. However, in the right panel of Fig. 6 NO_y increases over the last 1 to 2 days of transport. How can this be?

We thank the referee for pointing out the unexpected increase of NO_y during the last 1 to 2 days of transport. This turned out to be an error in the calculation of upwind folded quantity (UFQ, defined in Sect 2.4). The mixing ratios used to compute the UFQs were saved in two different GEOS-Chem simulations, one for 2009 and one for 2010. We initially processed the 2009 event and when we processed the 2010 event, we assumed the GEOS-Chem files were formatted and organized in the same manner as the 2009 files. Upon inspection of the files for this response, we found that the GEOS-Chem files for 2010 were formatted slightly different from 2009, which resulted in a mismatch in the timing of the FLEXPART retroplume and the GEOS-Chem plume. We have fixed this problem and revised Fig. 6 e-h accordingly. In the updated Fig 6, NO_y decreases slowly for the last several days of transport, which correctly reflects photochemical loss of NO_y species far from pollution source regions. As part of this response, we also conducted careful examination of our processing programs for both events and confirmed that there was no issue with the 2009 data. In the revised manuscript, we believe that all figures correctly reflect simulation results. Fig. 6 has been updated in the revised manuscript.

- The authors note that PAN increases during the 3rd day of transport in the left panel of Fig. 6, and suggest that this is due to NO_x conversion to PAN. However, PAN increases by a significantly greater amount than NO_x decreases. How can this be?

In general, we agree with the reviewer's assessment that the PAN and NO_x behavior is not entirely consistent with a perfectly Lagrangian view of the plume. We attribute this discrepancy to the inherent issues, as outlined above, that make the results "semi-Lagrangian" rather than perfectly Lagrangian. Here, we show additional profiles of PAN and NO_x for the corresponding time steps to demonstrate the issue for this specific case. Fig. R1 below shows GEOS-Chem chemical profiles and vertical distribution of the FLEXPART retroplume at the three time steps during the UFQ PAN increase on the last few days of transport. From the time step of Fig. R1a (9:00 UTC on June 11) to R1c (9:00 UTC on June 12), the CO profile shows the pollution plume was lifted from 2.0 km to about 3.5 km a.s.l. The change in ozone and PAN profiles are nearly consistent with the CO profile, showing slight increase at the same altitude. However, the NO_x profiles fail to show similar trends because of a potential cloud layer formed in the low troposphere (RH profile in Fig. R1a). There was no NO_x enhancement at the pollution plume height in the first time step (Fig. R1a), likely due to efficient deposition of NO_x in clouds. Two time steps later in Fig. R1c, the NO_x profile started to show an increase at 1.8 km a.s.l. because the cloud layer became weaker at this height. The NO_x enhancement, which should be part of the entire plume, was only observed in the lower portion of the plume because of wet deposition during lifting. This could cause a problem in the Lagrangian approach. Owing to a slight transport discrepancy, the FLEXPART retroplume mostly sampled the upper part of the plume for all three steps shown and was able to cover the concentrated CO and ozone in GEOS-Chem quite well, but possibly missed what happened in the lower part. In the upper part of the plume, NO_x had already been transformed to PAN or washed out in the cloud during plume lifting, so a small change in NO_x was observed in the folded results. The lower part of the plume, where significant NO_x change can be expected, was not sampled by the retroplume because of the disagreement in convective transport of the two models. Thus, greater PAN increase than NO_x decrease was reflected in the Lagrangian approach results in this case.

With regards to this issue, on pg. 15160, line 8, before “After being lifted from the PBL…”, we added

> “The increase in PAN was found to be much higher than the decrease in NO_x during this lifting, which may appear inconsistent if it is assumed PAN is formed primarily from NO_x destruction. When PAN reached its highest mixing ratio at 12:00 on 12 June, due to a slight discrepancy in convection in the two models, the FLEXPART retroplume profile did not entirely match the GEOS-Chem plume profile and only sampled in the upper part of the plume (see Fig. 7, Column 1, Panel b). During lifting, the GEOS-Chem plume encountered a potential cloud layer (see RH in Fig. 6, Panel d). As a consequence, the FLEXPART retroplume, which was concentrated above the potential cloud layer, sampled the upper part of the plume where NO_x had already been transformed to PAN or washed out during lifting. The lower part of the plume, where significant NO_x change could be expected, was not sampled by the retroplume because of the disagreement in convective transport in the models. Thus, the change in NO_x in the folded results may have been underestimated. CO and ozone, which are more stable than NO_x, were unaffected by the potential cloud layer on the short timescale, and the retroplume corresponded well to the layers in which CO and ozone were elevated, so the effects on the folded results of CO and ozone were small.”

- pg. 15162, lines 4-5: The authors state that "RH was higher (in Event 6) than in Event 2 (60–80% versus 40–60%) due to transport at lower altitude." What sense does this make? Temperature generally decreases with altitude, and RH increases as temperature decreases. Perhaps the authors should discuss absolute water vapor concentrations, since they should be conserved under Lagrangian transport in the absence of precipitation or mixing with other air masses. However, temperature and RH do not co-vary in the manner that I would expect.

We agree that our statements about RH, temperature and transport height were unclear and misleading. We think it is more reasonable to use RH for the following reasons: a higher RH in the folded results means that more of a plume may interact with clouds, which could increase wet deposition. The higher RH in Event 6 indicates that the plume may not be lifted entirely above the boundary layer (retroplume shown in Fig. 6h). Higher temperature and active convection in the boundary layer may cause rapid chemical loss in the plume. For clarification, we replaced the original sentences on pg. 15162, lines 4-5, which stated, “RH was higher (in Event 6) than in Event 2 (60–80% versus 40–60%) …… in which warm temperature and high concentrations of water vapor accelerated destruction of ozone and removal of ozone precursors.” with,

> “RH was higher in Event 6 (60–80%) than in Event 2 (40–60%), which indicates a

greater part of the Event 6 plume may have interacted with a cloud layer during transport and thus was not lifted above the boundary layer. Compared to Event 2, these meteorological conditions in the boundary layer may have enhanced destruction of ozone and removal of ozone precursors."

- The RH behavior in Fig. 6 (especially in Event 2) does not seem realistic to me. During lofting of boundary layer air in a warm conveyer belt, RH is expected to reach 100% due to adiabatic cooling, leading to cloud formation and likely precipitation. However, this is not reproduced in the Lagrangian calculations, and the authors do not discuss these issues.

  The revision and discussion given above also addressed this issue. RH is expected to reach 100% in the cloud layer and in a warm conveyor belt, however, (1) the high water content in the cloud layer may get averaged out in GEOS-Chem grid cells due to numerical diffusion (see the GEOS-Chem RH profiles in Fig R1, the highest RH observed in the FT was about 95%), and (2) even though the majority of the retroplume was found in the cloud layer, there could be still a portion of the retroplume that sampled air outside the cloud layer (see the broad vertical distribution of retroplume in Fig. R1). Thus, on the contrary, we expect that RH should not have reached 100% in Fig. 6.

In summary, something seems significantly wrong in the results of the Lagrangian calculations. Before proceeding with a more detailed discussion, the authors must demonstrate that their Lagrangian analysis is indeed performed correctly.

We thank the referee for the comments and suggestions which helped to improve the description and discussion of the method and fixed a calculation error in our results. With the advanced discussion here and modifications in the manuscript, we hope that we clarified the referee's concerns regarding the semi-Lagrangian method, and that we have demonstrated the validity of the modeling results and conclusions.

2) This paper does not adequately treat the complex interplay of atmospheric processes that affect the ozone versus CO correlation in the atmosphere. There are two important papers that should be reviewed and carefully considered in developing the analysis presented in this paper. *Kim et al.* [2013] interpret satellite-derived ozone–CO correlations with the GEOS-Chem chemical transport model (one of the models used in the present work). They point out the importance of stratospheric ozone, lightning NO_x, and biogenic influences in affecting this correlation. In general, the ozone–CO correlation results from PMO must be considered in the context of this work.

We thank the referee for directing us to two recent works on topics related to our manuscript. The referee cited the work from *Kim et al.* (2013) and suspects the lack of consideration of different sources of ozone and ozone precursors in the ozone–CO correlations analysis. We were aware of the impacts of the various sources of ozone and ozone precursors during our work, but the ozone-CO correlation analysis we did was built upon specific time periods and transport, and we avoided many of these complex influences by extracting events that excluded impacts from these other sources, as described in Sect. 3.1 in the manuscript. This manuscript was a follow-up study of *Honrath et al.*, (2004) and focused on elevated d[O_3]/d[CO] observed during specific transport events from North America. The analysis of ozone–CO correlations was built upon carefully selected events. This approach narrowed the ozone–CO analyses to particular periods when plumes contained anthropogenic pollution from North America. For example, the efforts we made in Sect. 3.1.3-5 allowed us to avoid other sources such as stratospheric ozone and focus on events that were affected by N.A. anthropogenic sources only. We were also able to calculate the percentile of lightning NO_x to total NO_x (< 10%) for the two studied events. This approach is fundamentally different from that employed by *Kim et al.* (2013). *Kim et al.* (2013) studied ozone-CO correlation in bulk datasets, covering large areas and altitude ranges on a seasonal basis, and investigated model results and satellite data for different regions. They included all data, regardless of the source of the observed pollution. As a result, in each scenario they studied, there may have been contributions from different ozone sources. For the reasons stated above, we believe that no change to the manuscript is warranted in this regard.

With regard to ozone–CO correlations for specific plumes *Yokelson et al.* [2013] point out the difficulty of simply interpreting correlations between any two atmospheric chemical species. Any observed correlation such as discussed in the present paper is actually a mixing curve between two different air masses. The correlation can only be used to infer information about sources of species if the two air masses are identical except for the influence of a particular source. This is certainly not the case in Figure 10 of the present paper, where the authors have chosen to examine the correlation based on mixing of pollution plumes from North America with some hypothesized "background" air mass. For the concentrations in this "background" air they chose the lowest 10% of all observed ozone and CO concentrations in a 3-month summertime period. This "background" air will very likely represent air that has circulated over the North Atlantic for many days. It will not be representative of "background" air over the North American continent where the pollution plume originated. Hence, the observed correlations at PMO cannot be simply interpreted as the authors attempt to do in Figure 10. I suspect that the ozone-CO correlations at PMO really provide little information regarding ozone production in plumes of anthropogenic emissions transported to PMO, and that the authors must approach this problems from a different perspective.

We thank the referee for directing us to another recent and informative paper, which discusses the validity of normalized mixing ratios (e.g., d[O_3]/d[CO]). The long lifetime of CO in the troposphere makes it a widely-used tracer of combustion processes. Usually, when a pollution plume mixes with identical background air, the change in CO mixing ratio in the plume is not affected much by chemistry but only by dilution. Hence, the normalized ratio d[O_3]/d[CO] in the plume should reflect ozone production/loss during transport. Both the referee and *Yokelson et al.* (2013) are aware of a potential issue in calculation of normalized mixing ratios such as d[O_3]/d[CO]. Studies of normalized mixing ratios are built upon the assumption that plumes of pollution are mixed with the same background air. Only under this assumption can a normalized mixing ratio be derived by connecting the concentration of pollution in the plume and a background level, which indicates a dilution process. The referee used the work by *Yokelson et al.* (2013) to point out that if a plume is mixed with different background air sources during transport, a regression line that connects the concentration of pollution in the plume and a single "background" can lead to unrepresentative mixing and a flawed analysis of ozone-CO correlations. We generally agree with the idea, but for the following reasons, we still believe that our analysis of d[O_3]/d[CO] is not undermined by this problem and that the corresponding analysis of ozone production during transport is valid.

According to the FLEXPART folded retroplumes in Fig. 3, pollution plumes were exported from the continental region of North America to the North Atlantic region about five days before they arrived at PMO. During the rest of the transport, the plumes mainly mixed with adjacent air over the North Atlantic. Background levels of ozone and CO could be different between the air over North America and that over the North Atlantic, but the background levels of CO and ozone in different regions over the North Atlantic should be similar because there are no emission sources of CO and ozone precursors over the ocean. For the transport, which occurred mostly over the North Atlantic region, it was reasonable to use the mixing between a pollution plume from North America and a background level over the North Atlantic to mimic the mixing part of d[O_3]/d[CO]. Because PMO is the only observatory that provides continuous and long-term measurements in the mid-latitude North Atlantic regions, we think the PMO dataset is the best one from which to extract North Atlantic background CO and ozone levels.

For the reasons given above, we believe the line between pollution concentrations in the plume and the background over the North Atlantic appropriately reflects the potential mixing process during transport from North America to PMO. However, the selection of the background and plume values in Fig. 10 was questioned by the referee. In the manuscript, we originally used the lowest 10% of all observed ozone and CO concentrations in a 3-month summertime period as the background. This estimation of background is coarse because low levels of ozone and CO can be caused by transport from tropical regions, where mixing ratios of pollution are significantly lower than those in mid-latitude regions. To address this issue, in the revised manuscript we used two new criteria to identify CO and ozone measurements as North Atlantic background values:
(1) Retroplumes should have more than 50% of its residence time over the North Atlantic region (defined by latitude from 30 °to 48 °and longitude from -60 °to -15 °) at ten days upwind from PMO.
(2) Retroplumes should have more than 80% of their residence time under a vertical height of 5 km at ten days upwind from PMO.
The first criterion ensures that the CO and ozone observed during this period were aged mid-latitude North Atlantic air given a typical transport time from North America to PMO is approximately 6-7 days (*Honrath et al.* 2004). The second criterion rules out stratospheric intrusion and any transport from the upper troposphere, where ozone is much higher. CO and ozone values in retroplumes sampled according to these criteria were averaged and used as background levels in the revised Fig. 10 and accompanying discussion. With regards to ozone

and CO mixing ratios in pollution plumes, we also made some improvements during the revision. We replaced the outdated observations listed in Table 2 by MOZAIC flight measurements in 2008, 2009 and 2010. Please refer to the responses to Referee #1 for detailed modifications.

In this comment, the referee used a reference to point out that the composition change of background air could invalidate the analysis of normalized mixing ratios. In the discussion above, we tried to demonstrate that the selection of the North Atlantic background was appropriate for our study and that we have avoided the issue of a composition change in the background air. In addition, during the revision process we incorporated better datasets to make our analysis in Fig. 10 more robust. By providing the explanations and revisions above, we hope to have fully addressed this concern from the referee.

Relatively Minor Concerns:

1) There are many typos (e.g. pg. 15146, line 11: What does "with 1 horizontal resolution" mean) and minor misusages of English. The paper requires a careful editing by a native English speaker before publication.

The manuscript has been carefully edited for English language usage.

2) pg. 15153, lines 15-20: The seasonality of the dO_3/dCO slope should be discussed. Negative slopes may be expected in wintertime pollution plumes, at least near source regions.

PMO is usually not operated during wintertime so this study focused on summertime transport. More discussion of $d[O_3]/d[CO]$ in summer and spring was added on page 15151, lines 5-10.

3) pg. 15151, line 10: The term "dividing streamline" is used here, but a different term is used in
Fig. 1; consistency would be good here.

We thank the referee for pointing out this inconsistency in the paper. “Dividing streamline” is now used consistently in the revised manuscript.

4) pg. 15154, lines 3-5: The authors note that "Significant ozone enhancement is observed in all events, with $d[O_3]/d[CO]$ values ranging from 0.85 to 2.28, indicating different photochemical processes caused by various characteristics of transport." However, they fail to note the important influence of comparison between air masses of different origin. This seems to be the root cause of the second major concern noted above.

We agree that the statement was incorrectly written. We replaced this sentence with

> “A range in $d[O_3]/d[CO]$ values (from 0.85 to 2.28) was found for the eight events. Our criteria selected events with significant impacts from anthropogenic or biomass burning emissions.”

However, this didn’t affect the analysis in the rest of the paper because only two events affected by anthropogenic emissions were studied in detail.

5) I am concerned about the results presented in Section 3.3.3 and Fig. 5, which seem to show that the model derived correlations between hydrocarbon ratios evolve as expected from chemical kinetics unaffected by air mass mixing. Yet Helmig et al. [2008] and Honrath et al. [2008] clearly show that mixing of air masses strongly affects correlations between hydrocarbon ratios actually measured at PMO. How can the analysis in Section 3.3.3 be consistent with the measurements reported in these two papers?

We believe the referee has misinterpreted these results. The papers by *Helmig et al.* (2008) and *Honrath et al.* (2008) investigated NMHC ratios in a perspective different from the present manuscript. The work in the two papers used measurements of NMHC at PMO, which represented observations of all kinds of aged plumes after transport. Some plumes could certainly be affected by mixing because they might undergo different types of transport (e.g., transport in the boundary layer vs. free troposphere). It was shown in the previous work that the correlations between the natural logarithms of NMHC were distributed across a range bounded by mixing-only and kinetic-only scenarios. In the current manuscript, we showed a semi-Lagrangian view of NMHC evolution in the plume during transport (Fig. 5; vs. observations at PMO in the previous work). The selected plumes were more compacted compared to the unclassified data reported in the previous work, so the slopes for these two events can be expected to be closer to the kinetic-only scenario.

Second, the correlations between the natural logarithms of NMHC were affected by mixing for the two events studied in the present manuscript, only not very intensively because we selected events that exhibited direct transport from North America to PMO. As we discussed on pg 15157, line 25, the transport trajectory of Event 2 was more compressed than that of Event 6, which explains why the regression slope of the natural logarithms of NMHC for Event 2 was closer to the kinetic-only scenario. However, in general, both events exhibited highly compressed transport due to the selection criteria we applied, so the mixing effect is not very great.

6) pg. 15159, lines 22-23: The authors state that "oxidized nitrogen species levels also decreased quickly due to short photochemical lifetime in the FT." I do not believe that this statement is correct. NO_x has a fairly short lifetime in the FT, but certainly longer than in the boundary layer. PAN and NO_y have long lifetimes in the FT.

We thank the referee for pointing out this error. We meant a relatively "shorter lifetime as compared to CO". In the revised manuscript, we replaced the sentence with

> "…levels of oxidized nitrogen species decreased quicker due to relatively shorter photochemical lifetime as compared to CO in the FT."

7) pg. 15166, lines 11-12: References should be given for the values measured during the ICARTT campaign.

The relevant references have been added.

References:

Helmig, D., D. M. Tanner, R. E. Honrath, R. C. Owen, and D. D. Parrish (2008), Nonmethane hydrocarbons at Pico Mountain, Azores: 1. Oxidation chemistry in the North Atlantic region, J. Geophys. Res., 113, D20S91, doi:10.1029/2007JD008930.

Honrath, R. E., Helmig, D., Owen, R. C., Parrish, D. D., and Tanner, D. M. (2008), Nonmethane hydrocarbons at Pico Mountain, Azores: 2. Event-specific analyses of the impacts of mixing and photochemistry on hydrocarbon ratios, J. Geophys. Res., 113, D20S92, doi:10.1029/2008JD009832.

Kim, P. S., D. J. Jacob, X. Liu, J. X. Warner, K. Yang and K. Chance (2013), Global ozone–CO correlations from OMI and AIRS: constraints on tropospheric ozone sources, *Atmos. Chem. Phys. Discuss.*, *13*, 8901–8937.

Yokelson, R.J., M.O. Andreae, and S. K. Akagi (2013), Technical Note: Pitfalls with the use of enhancement ratios or normalized excess mixing ratios measured in plumes to characterize pollution sources and aging, *Atmos. Meas. Tech. Discuss.*, *6*, 4077–4085.

Reference cited during the authors' revision:

Honrath, R. E., Owen, R. C., Val Martin, M., Reid, J. S., Lapina, K., Fialho, P., Dziobak, M. P., Kleissl, J., and Westphal, D. L.: Regional and hemispheric impacts of anthropogenic and biomass burning emissions on summertime CO and O3 in the North Atlantic lower free troposphere, Journal of Geophysical Research-Atmospheres, 109, D2431010.1029/2004jd005147, 2004.

Owen, R. C., and Honrath, R. E.: Technical note: a new method for the Lagrangian tracking of pollution plumes from source to receptor using gridded model output, Atmospheric Chemistry and Physics, 9, 2577-2595, 2009.

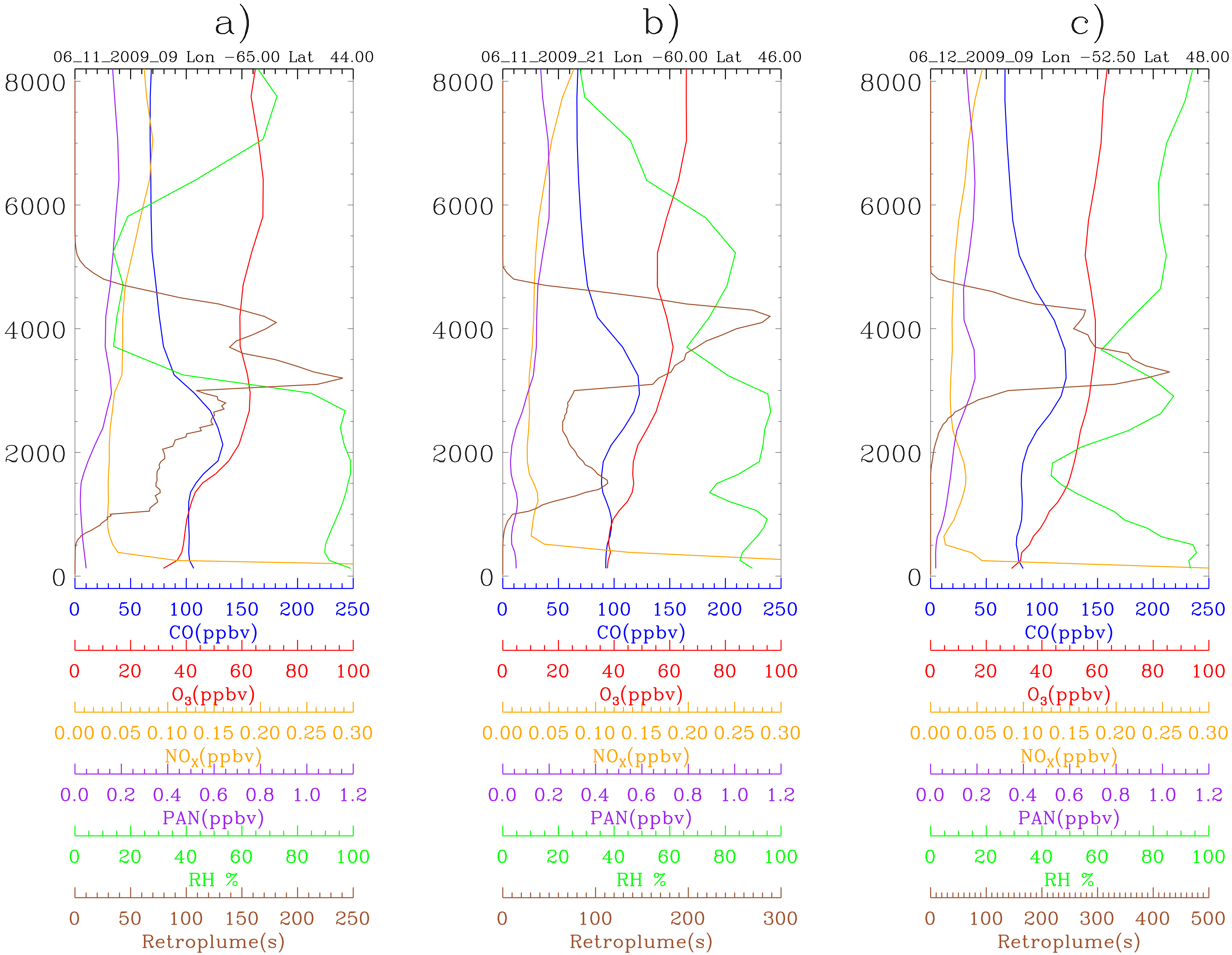
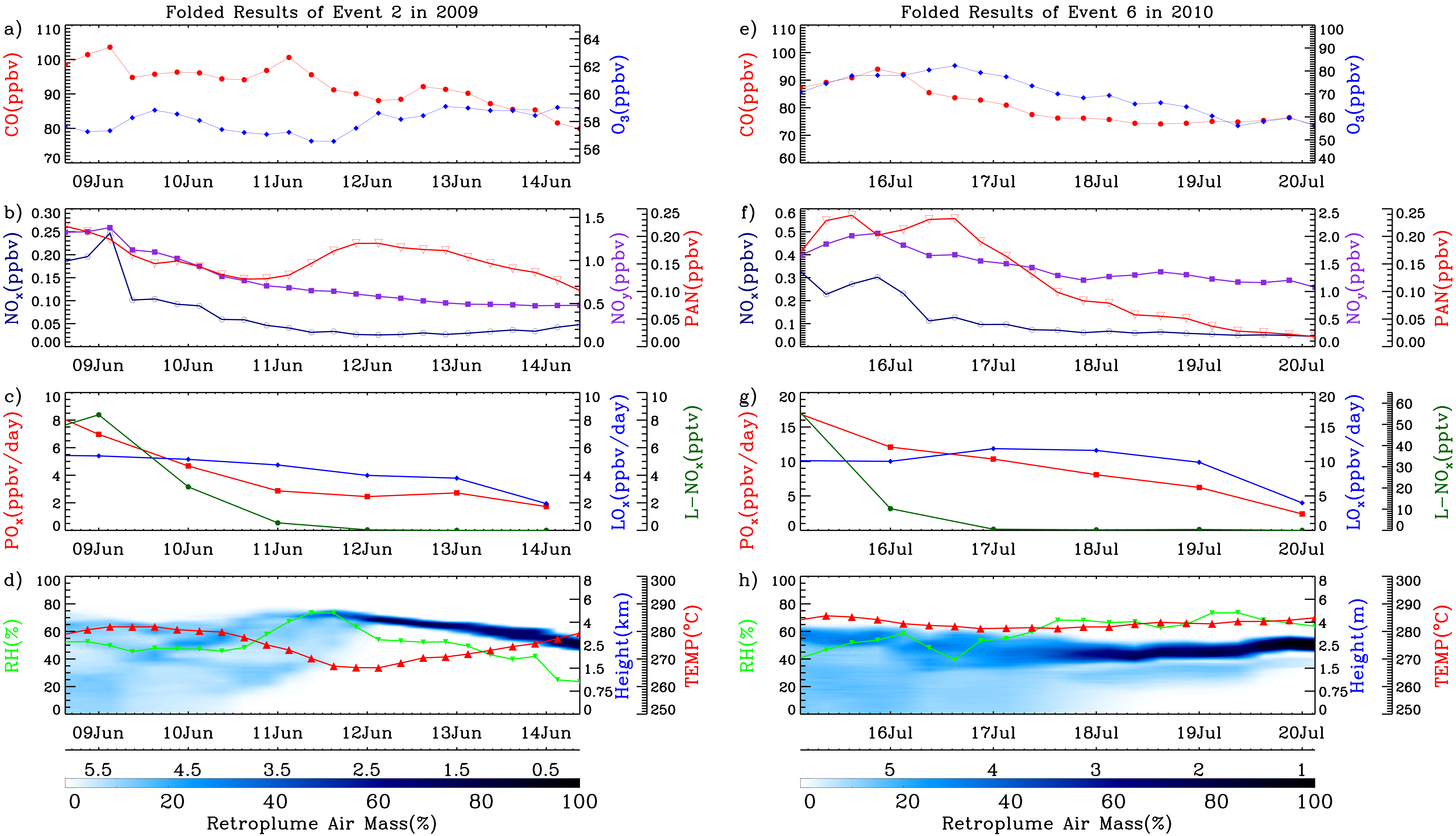

a)
06_11_2009_09 Lon −65.00 Lat 44.00
b)
06_11_2009_21 Lon −60.00 Lat 46.00
c)
06_12_2009_09 Lon −52.50 Lat 48.00
8000
6000
4000
2000
0
0 50 100 150 200 250
CO(ppbv)
0 20 40 60 80 100
O_3(ppbv)
0.00 0.05 0.10 0.15 0.20 0.25 0.30
NO_x(ppbv)
0.0 0.2 0.4 0.6 0.8 1.0 1.2
PAN(ppbv)
0 20 40 60 80 100
RH %
0 50 100 150 200 250
Retroplume(s)
0 100 200 300
Retroplume(s)
0 100 200 300 400 500
Retroplume(s)

Figure R1. GEOS-Chem profiles of tracer gases and FLEXPART retroplumes at three upwind times when the Event 2 plume was lifted into the free troposphere on 11 June 2009 (UTC). These three times were selected to show the vertical convection of the pollution plume in GEOS-Chem and FLEXPART. Discussion is given in the text to interpret the significant increase of PAN in the folded results shown in Fig. 6 in the manuscript.


Folded Results of Event 2 in 2009
Folded Results of Event 6 in 2010
a)
CO(ppbv)
O$_3$(ppbv)
110
100
90
80
70
64
62
60
58
56
09Jun
10Jun
11Jun
12Jun
13Jun
14Jun
b)
NO$_x$(ppbv)
NO$_y$(ppbv)
PAN(ppbv)
0.30
0.25
0.20
0.15
0.10
0.05
0.00
1.5
1.0
0.5
0.0
c)
PO$_x$(ppbv/day)
LO$_x$(ppbv/day)
L−NO$_x$(pptv)
10
8
6
4
2
0
d)
RH(%)
Height(km)
TEMP(°C)
100
80
60
40
20
0
8
6
4
2.5
1.5
0.75
300
290
280
270
260
250
5.5
4.5
3.5
2.5
1.5
0.5
0
20
40
60
80
100
Retroplume Air Mass(%)
e)
CO(ppbv)
O$_3$(ppbv)
16Jul
17Jul
18Jul
19Jul
20Jul
f)
NO$_x$(ppbv)
NO$_y$(ppbv)
PAN(ppbv)
0.6
0.5
0.4
0.3
0.2
0.1
0.0
2.5
2.0
1.5
1.0
0.5
0.0
g)
PO$_x$(ppbv/day)
LO$_x$(ppbv/day)
L−NO$_x$(pptv)
20
15
10
5
0
60
50
40
30
h)
RH(%)
Height(m)
TEMP(°C)
5
4
3
2
1
Retroplume Air Mass(%)

Revised Fig. 6. Folded results (UFQs) of pollution plumes at each model time step during Event 2 (left column) and 6 (right column). Data color corresponds to the respective y-axes. Six-hour averaged UFQs of tracer gases are shown in a), b), e) and f). Folded daily averaged UFQs of ozone production (POx) and loss (LOx) rates and lightning NO_x (L-NO_x) are shown in c) and g). FLEXPART retroplume, temperature and RH in the folded results are shown in d) and h), with dual x-axes for date in UTC and upwind time in days.