Review of "A Lagrangian view of ozone production tendency in North American outflow in summers 2009 and 2010" by B. Zhang et al.

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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 mid-latitudes. 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.

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:

   - In the absence of loss due to precipitation scavenging or input from lightning, NOy 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 NOy increases over the last 1 to 2 days of transport. How can this be?
   - 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 NOx conversion to PAN. However, PAN increases by a significantly greater amount than NOx decreases. How can this be?
   - 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.
   - 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.

   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.

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 NOx, 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.

   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.

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.

2) pg. 15153, lines 15-20: The seasonality of the dO3/dCO slope should be discussed. Negative slopes may be expected in wintertime pollution plumes, at least near source regions.

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.

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.

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?

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.

NOx has a fairly short lifetime in the FT, but certainly longer than in the boundary layer. PAN and NOy have long lifetimes in the FT.

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

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.

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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.