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Atmospheric Chemistry and Physics Discussions

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

Anonymous Referee #1

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This manuscript presents a new modeling technique that builds on the methods of Owen and Honrath [2009] to fold FLEXPART retroplumes with GEOS-Chem forward simulations to isolate the chemical evolution of pollution plumes as they are transported from the eastern USA to Pico Mountain Observatory in the remote eastern North Atlantic Ocean. Overall I find the modeling technique to be sound and of value to the scientific community. However I have strong reservations regarding the overall conclusions. While I think it is very possible that the O3/CO relationship can be driven as much by CO loss as by ozone production/destruction (based on the previous results of Real et al. 2008) I worry that the present study has reached the same conclusion due

to some faulty assumptions. I elaborate on this concern below and also provide additional comments/suggestions that would improve the analysis. Without further analysis I have no confidence in the main conclusions of this manuscript. However, I think that if the authors revise their analysis as outlined below they will produce much more reliable estimates of the evolution of ozone and CO between the USA and PMO. My recommendation to the editor is that this paper be sent back to the authors for a major revision.

Major comments:

The main conclusions of the analysis are drawn from Figure 10 which explores the mixing process between polluted air masses that travel from the eastern US to PMO. The analysis assumes that the pollution plumes from the USA mix with background air which the authors decide is characterized by the lowest 10% of ozone and CO mixing ratios measured at PMO during the summer. But why would the plumes only mix with clean "background" conditions. Couldn't the plumes just as easily mix with moderately polluted air? And where in the atmosphere are these clean "background conditions" found? Aged mid-latitude air does not have such low ozone (17 ppbv) and CO (63 ppbv) mixing ratios. Rather, these mixing ratios are typical of the tropical lower troposphere, so if they are found in the mid-latitudes they are associated with tropical air masses that have been recently advected into the mid-latitudes. If the authors ran FLEXPART retroplumes for these "background" events I am confident that they would show a tropical origin. So basically the authors are assuming that whenever a pollution plume leaves the eastern USA it mixes with tropical air. This might be true some of the time, but it's far more likely that the plume would mix with aged mid-latitude air which has much higher ozone and CO mixing ratios. By examining the spatial extent of the retroplumes in Figure 3 we can get an idea of the range of air masses that mixed to produce the polluted air mass sampled at PMO. Neither of the retroplumes in Figure 3 indicates a contribution from tropical air. Therefore the authors need to seriously reconsider how they characterize background air. They should provide a range of

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background conditions and then see how robust their conclusions are.

Another problem with this analysis is that there is absolutely no evaluation of GEOS-Chem estimated ozone and CO over the eastern USA. If we don't know that the model is reasonably correct at the start of the pollution export episode, how can we have confidence that it correctly reproduces the chemical evolution of the plume? The authors state that 1) in situ measurements for model evaluation are not available, and 2) conclude that it is acceptable to instead use ozone and CO measurements from field missions conducted in 1993 and 2004 and adjust the CO data to account for emissions changes that have occurred over the 1993-2010 time period. These assumptions are incorrect and greatly lower my confidence in the conclusions of the paper. 1) There are plenty of in situ measurements across the eastern USA to evaluate GEOS-Chem. There are many rural ozone sites in the National Park Service and CASTNET databases (many at high elevations) that are suitable for evaluating a course model such as GEOS-Chem: http://epa.gov/castnet/javaweb/index.html http://ard-request.air-resource.com/ TES ozone and CO retrievals for the mid- and lower troposphere can also be used above the USA and the North Atlantic. Also, MOZAIC aircraft profiles are available, as discussed below. 2) Trying to characterize ozone and CO above the eastern US in 2009 and 2010 using data from 1993 and 2004 is a bad idea. Even though the authors acknowledge that emissions have changed over this time period their method of adjusting the measured CO to account for the change is not acceptable when they could produce a very nice summertime ozone/CO climatology for the eastern US using MOZAIC ozone and CO profiles from 2008-2011, as described below. Furthermore, it's not just CO that has decreased greatly, but so have NOx and VOCs which have greatly changed the photochemistry over the eastern US and resulted in very large decreases in ozone (see Cooper et al. 2012, and He et al. 2013). So ozone and CO from 1993 and 2004 cannot be used to characterize the eastern USA in 2009 and 2010, and the authors need to use the freely available MOZAIC data.

Cooper et al. (2012), Long-term ozone trends at rural ozone monitoring

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sites across the United States, 1990–2010, J. Geophys. Res., 117, D22307, doi:10.1029/2012JD018261.

He et al. (2013), Trends in emissions and concentrations of air pollutants in the lower troposphere in the Baltimore/Washington airshed from 1997 to 2011, Atmos. Chem. Phys. Discuss., 13, 3135-3178.

The MOZAIC program (now called IAGOS) has used commercial aircraft to measure ozone around the globe since 1994 and CO since 2001. I checked the IAGOS database: http://www.iagos.fr/web/rubrique40.html and there are plenty of flights to the eastern US (Boston, Philadelphia, Detroit, Atlanta) during the summers of 2008-2011. These ozone and CO profiles can be used to produce climatological ozone and CO values for the eastern US lower troposphere. These values need to replace the extremely outdated ozone and CO values from 2004 and 1993 that are currently used in this manuscript. Furthermore the MOZAIC profiles from June 2009 and July 2010 can be used to evaluate GEOS-Chem's estimates of ozone and CO exported from the US in the two case studies examined by this manuscript.

Minor comments:

The first few lines of the Introduction discuss ozone properties but are not referenced. Please provide some overview references.

Line 6 page 15146 What is the base year for the EDGAR inventory?

Line 11 page 15146 GFS winds are used at 1 degree resolution. But GFS winds have been available at half degree resolution for years. Why not use the half degree winds?

Line 27 page 15146 Here and throughout the paper the term "outputs' is used, which is not a word. Instead please use "output" or some other expression.

Line 24 page 15147 Here it says the model was only run for January-July 2010. So where does the 2009 model output come from?

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Line 16 page 15148 I'm not sure what is meant by "entrywise"

Line 10 page 15153 Here model data in the middle of the North Atlantic is used to determine when boundary layer air rises to PMO. Why use coarse, unreliable model data in the middle of the Atlantic when you could easily use in situ specific humidity time series to tell when moist and relatively warm boundary layer air is advected to the site?

Line 20 page 15153 If you ran GEOS –Chem at 2x2.5 degrees, why would you extract ozone and CO from a different model run at 4x5 degrees?

Line 15 page 15155 Here the authors say that they identified warm conveyor belts using NOAA daily weather maps. But these maps only show surface fronts and 500 hPa isoheights. They do not show WCBs. The only way to say for sure if a WCB was present is to check archived satellite images at: http://locust.mmm.ucar.edu/imagearchive/

Page 15158 Instead of combing FLEXPART with GEOS-Chem, why not just use the GEOS-Chem adjoint [Zhang et al., 2009] to achieve the same results?

Zhang, L., D. J. Jacob, M. Kopacz, D. K. Henze, K. Singh, and D. A. Jaffe (2009), Intercontinental source attribution of ozone pollution at western U.S. sites using an adjoint method, Geophys. Res. Lett., 36, L11810, doi:10.1029/2009GL037950.

Two other papers that need to be considered when discussing the background of the O3/CO relationship are:

Chin et al. (1994), Relationship of ozone and carbon monoxide over North America, J. Geophys. Res., 99, 14,565-14,573.

Cooper et al., PROPHET 1998 meteorological overview and air-mass classification, J. Geophys. Res., 106, 24,289-24,299.

Chin et al. noted that a typical ozone/CO slope in the USA is 0.3 and attributed this to photochemistry. But Cooper et al. showed that transport alone could also produce a

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slope of 0.3, as the authors of this manuscript mention on lines 17-20, page 15151.

Table 2 There are quite a few other papers that discuss transport of ozone and CO to the North Atlantic, though not all in summer. Was the intention that this table just focus on summer events? A paper that was omitted is:

Berkowitz et al. (1996), Synoptic patterns associated with the flux of excess ozone to the western North Atlantic, J. Geophys Res., 101, 28923-28933.

And a good springtime study is:

Prados et al. (1999), Transport of ozone and pollutants from North America to the North Atlantic Ocean during the 1996 AEROCE intensive, J. Geophys. Res., 104,

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Interactive comment on Atmos. Chem. Phys. Discuss., 13, 15141, 2013.