

## Response to Reviewer's comments on He et al. 2013 ACPD

We thank the anonymous reviewer for thoroughly reading our manuscript and providing helpful comments and suggestions. The detailed responses to major points are listed below (text in italics shows the reviewer's comments, and the text in blue is our response):

*Overall I find the science and analysis conducted for this manuscript to be acceptable (with a few minor exceptions described below) and I think that the information provided will be valuable to the scientific community. I recommend that the authors conduct a major revision of the manuscript according to my comments below.*

*Before I begin my detailed review of the manuscript I will first list two general complaints.*

*1) My first complaint is directed towards the ACPD policy on copy editing and I ask the editor to pass my comment on to the relevant department. I have been a peer-reviewer for ACPD for 10 years and I have complained many, many times in the past that some of the figures are too small to read. For this paper Figures 2 and 7 are far too small. Illegible figures make the review process very difficult and ACPD needs to implement procedures that ensure all figures are legible. This is a complaint that I rarely make to other journals such as JGR, Atmospheric Environment or Nature.*

Response: We sympathize. The figures were submitted in PostScript format with a single plot per page. When the paper was formatted and published in ACPD, several plots, for instance Figure 2 a, b and c, were condensed onto the same page. Although the figures can be magnified using a PDF reader, we agree that they are hard to read at normal size, especially when printed. We will work with ACP staff to provide more size for the figures if this manuscript proceeds to ACP.

*2) My second complaint is directed towards the co-authors of this manuscript. The standard procedure for submitting a manuscript to a peer-reviewed journal such as ACPD is that all co-authors read the manuscript and correct any errors prior to submittal. The manuscript is not to be submitted until all co-authors approve of the final version. It is clear to me that the co-authors of this manuscript did not fulfill their responsibilities in terms of proof-reading the manuscript. The result is a paper that is riddled with grammatical errors and also contains some factual errors that easily could have been corrected. This dereliction of duty is completely unacceptable and places an undue burden on the editor and referees; it is also a disservice to the lead author. I will not spend my time correcting the many grammatical errors as this is the responsibility of the co-authors. Should the editor ask me to re-review this paper at a later date I will decline if the co-authors have not performed their duty of correcting the manuscript. The editor will then have to find another referee which will delay the review process.*

Response: We apologize and all authors will scrutinize the manuscript before submission of the revised manuscript.

*In my comments below, if no explanation is given, please insert the recommended text into the appropriate place in the manuscript*

*Page 3137 line 4, change to: We examined observed and inventoried trace gas emissions,*

**Response:** We will follow this suggestion.

*Page 3137 line 9 Here and throughout the manuscript the use of the term “column contents” is not grammatically correct. A grammatically correct and more accurate description would be to say something like: “The decreasing trend of the lower tropospheric CO column is ~8.0 Dobson Units(DU) decade<sup>-1</sup>” where lower tropospheric is defined as 0-1500 m above ground level*

**Response:** Instead of ‘column content’, we will use ‘column abundance’ which is suggested by the Glossary of Meteorology (AMS)

*Page 3138 line 13 You need to be more specific about the contribution of the stratosphere to tropospheric ozone. In the upper troposphere the stratosphere is a major source of ozone. Also the reference to Levy et al. 1985 is out of date. There are far better estimates of strat-trop exchange such as: Stevenson et al., Multimodel ensemble simulations of present-day and near-future tropospheric ozone, JOURNAL OF GEOPHYSICAL RESEARCH, VOL. 111, D08301, doi:10.1029/2005JD006338, 2006*

**Response:** In this study, we examine ozone in the lower troposphere (the surface to 1.5 km), and had mentioned the upper troposphere as a discussion of background information. We will revise this sentence to emphasize the ‘lower troposphere’, and cite Stevenson et al. (2006).

*Page 3138 line 20 The reference to Oltmans et al 2006 is outdated. Instead please see: Oltmans, S. J., A.S. Lefohn, D. Shadwick, J.M. Harris, H.E. Scheel, I. Galbally, D.W. Tarasick, B.J. Johnson, E.-G. Brunke, H. Claude, G. Zeng, S. Nichol, F. Schmidlin, J. Davies, E. Cuevas, A. Redondas, H. Naoe, T. Nakano, T. Kawasato, 2013: Recent tropospheric ozone changes – A pattern dominated by slow or no growth. Atmospheric Environment, 67, 331-351.*

**Response:** We will follow this suggestion, and cite Oltmans et al. (2013) to this paragraph.

*Page 3138 line 20 The reference to Yorks et al 2009 is not appropriate as it is not about long term trends. See Oltmans et al 2013 and Cooper et al 2012. Then revise the following statement accordingly: “however long-term trends are not clearly observed”*

**Response:** We will follow this suggestion, and not cite Yorks et al. (2009) as a reference for long-term trends.

*Page 3138 line 24 The following paper should also be referenced: Parrish, D. D., D. B. Millet, and A. H. Goldstein (2009), Increasing ozone in marine boundary layer inflow at the west coasts of North America and Europe, Atmos. Chem. Phys., 9, 1303–1323, doi:10.5194/acp-9-1303-2009.*

**Response:** We will add Parrish et al. (2009) in this paragraph.

*Page 3138 line 25 Need to give more details on where the NAAQS exceedances occur. How bad are they?*

Response: We state that ozone is the major air pollution problem in the Baltimore/Washington nonattainment area, as described by the referenced EPA reports. Upon revision, we will add the sentence “the design value of daily maximum 8-hr ozone for Edgewood, MD (downwind of Baltimore) was 92 ppbv in 2011”.

*Page 3138 line 29 Which universities and agencies created RAMMPP?*

Response: We have revised this sentence: “For a better understanding of air quality, the Regional Atmospheric Measurement Modeling and Prediction Program (RAMMPP, <http://www.atmos.umd.edu/~RAMMPP>) at the University of Maryland was created to conduct state-of-the-art scientific research ...”

*Page 3139 line 14 The claim that previous studies focused on rural areas is not correct. The Lefohn studies relied on ozone monitors that were mainly in urban areas, as did the following paper: Fiore, A. M., D. J. Jacob, J. A. Logan, and J. H. Yin (1998), Longterm trends in ground level ozone over the contiguous United States, 1980–1995, J. Geophys. Res., 103(D1), 1471–1480, doi:10.1029/97JD03036.*

Response: We will follow this suggestion, and discuss the results of Lefohn et al and Fiore et al. in the revised manuscript.

*Page 3139 line 29 Use upwind and downwind instead of upstream and downstream*

Response: We will follow this suggestion, and use ‘upwind’ and ‘downwind’ in the revised manuscript.

*Page 3140 line 15 Why not also use NEI 1999?*

Response: We believe, based on procedural changes in monitoring, when compared with NEI 2002, 2005, and 2008, that the uncertainties in NEI1999 are relatively high by comparison (see [ftp://ftp.epa.gov/pub/EmisInventory/finalnei99ver3/haps/summaries/99nei\\_hap\\_potential\\_errors.mdb](ftp://ftp.epa.gov/pub/EmisInventory/finalnei99ver3/haps/summaries/99nei_hap_potential_errors.mdb)). We also focus on the significant changes before and after the SIP call, so use of NEI 2002,2005, and 2008 is appropriate.

*Page 3143 Here you use background when you should use baseline, as you did on page 3138. HTAP has defined the terms background and baseline, see the following reference: Dentener, F., T. Keating, and H. Akimoto (Eds.) (2011), Hemispheric Transport of Air Pollution 2010: Part A: Ozone and Particulate Matter, Air Pollut. Stud, vol. 17, U. N., New York.*

Response: We follow this suggestion, and will use ‘baseline’ in this manuscript.

*Page 3144 line 5 If a site is northwest of Baltimore, how can it be downwind?*

Response: This site is northeast of Baltimore. These unfortunately had been an error in the submitted manuscript which will be fixed upon revision.

*Page 3144 line 4 You need to provide a description of the trajectory calculations, briefly describing HYSPLIT and the type of meteorological data uses (resolution etc.)*

Response: This information is given in Table S4 of the auxiliary material.

*Page 3144 Here, or at some other point in the paper you need to cite earlier studies that establish the link between reduced powerplant emissions and reduced ozone in the eastern US: Frost, G., et al. (2006), Effects of changing power plant NO<sub>x</sub> emissions on ozone in the eastern United States: Proof of concept, J. Geophys. Res., 111, D12306, doi:10.1029/2005JD006354. Kim, S.-W., A. Heckel, S. A. McKeen, G. J. Frost, E.-Y. Hsie, M. K. Trainer, A. Richter, J. P. Burrows, S. E. Peckham, and G. A. Grell (2006), Satellite-observed U.S. power plant NO<sub>x</sub> emission reductions and their impact on air quality, Geophys. Res. Lett., 33, L22812, doi:10.1029/2006GL027749.*

Response: We thank the reviewer for providing these references. We will add them and Marufu et al. (2004) “The 2003 North American electrical blackout: An accidental experiment in atmospheric chemistry” to this manuscript.

*Page 3144 line 25 To be consistent with the use of the term “baseline” change this to say: (using 1997 emissions as the reference values)*

Response: We will follow this suggestion.

*Page 3145 line 7 You need to give more background information on the policies that led to the reduction in NO<sub>x</sub> emissions. The so-called “NO<sub>x</sub> SIP Call” may have paved the way for power plant NO<sub>x</sub> reductions but the actual program that reduced NO<sub>x</sub> is the NO<sub>x</sub> Budget Trading Program (NBP) later superseded by the Clean Air Interstate Rule (CAIR) NO<sub>x</sub> ozone season program. You need to replace the NO<sub>x</sub> SIP Call statements with NBP, and please also provide a brief description of NBP. For more details see the following references: Butler, T. J., F. M. Vermeylen, M. Rury, G. E. Likens, B. Lee, G. E. Bowker, and L. McCluney (2011), Response of ozone and nitrate to stationary source NO<sub>x</sub> emission reductions in the eastern USA, Atmos. Environ., 45, 1084–1094, doi:10.1016/j.atmosenv.2010.11.040. U.S. Environmental Protection Agency (2009), The NO<sub>x</sub> budget trading program: 2008 environmental results, report, Washington, D. C. [Available at [http://www.epa.gov/airmarkets/progress/NBP\\_3/NBP\\_2008\\_Environmental\\_Results.pdf](http://www.epa.gov/airmarkets/progress/NBP_3/NBP_2008_Environmental_Results.pdf)] <http://www.epa.gov/cair/>*

Response: We thank the reviewer for pointing out that the EPA SIP calls were the control measures implemented in 2003-2004, and the overall reduction of NO<sub>x</sub> emissions in the last 15 years has been regulated under NBP and CAIR. We will add discussion of these to the revised manuscript.

*Page 3146 line 2 Need a reference that states how ozone is affected by weather*

Response: We follow this suggestion, and add the EPA “Air quality criteria for ozone and related photochemical oxidants” (2006) as reference.

*Page 3146 line 2 Is this trend statistically significant? Please compare this finding to the Lefohn 2010 and Cooper et al 2012.*

Response: We used annual summer ozone levels in DC/MD/NOVA in the last 15 years, the R is -0.54, P = 0.046 with N = 14. These results show that the trend is statistically significant. We will add “P < 0.05” to Figure 4. The sentence will be revised to read “...long-term ozone measurements show large inter-annual variations, because ozone production is not only determined by emissions but also weather, especially temperature (EPA, 2006). A discernible decrease (~0.6 ppbv/year, Figure 4) is observed, suggesting a general decreasing trend of ambient ozone in the Baltimore/Washington area, similar to decreasing trends reported across the eastern U.S. (Lefohn et al., 2010; Cooper et al., 2012) ...”

*Page 3146 line 5 Are these CO monitors in urban areas?*

Response: Not all of them. Some of them are located in suburban and rural areas (see details in Figure S4 of the auxiliary material).

*Page 3146 line 20 Why scale by 4%?*

Response: As discussed on Page 3144, emissions are estimated from the annual national emission data, since long-term emission data for individual states are not available for instance 2003. To obtain emissions estimates for the Mid-Atlantic states, the national emissions must be scaled from county-scale emissions in NEI 2002, 2005, and 2008. The results are presented in Figure S2 of the auxiliary material, showing that the emissions in the Mid-Atlantic states are ~4% and 5% of the national NO<sub>x</sub> and CO emissions, respectively.

*Page 3147 line 11 Are these metric tons?*

Response: Yes. The original EPA data were in short tons, and we have converted them to metric tons.

*Page 3147 This paper has done a nice job of showing changes in air quality based on extensive measurements. Then the paper strays into some areas of speculation, such as the expected decrease in ozone based on NOx reductions and very vague ozone production efficiency values. This back-of-the-envelope calculation is too simplistic and not robust. This type of quantification is best left to chemical transport models. I recommend dropping this paragraph, which is not a loss to the paper as it is already strong from the excellent measurements.*

Response: We agree that our estimate presented here is simplified because the local OPE has not been reported, so we will delete this paragraph from this manuscript. However, our preliminary results show that chemical transport models might have significantly underestimated OPE. For instance, CMAQ has OPE values ~50% less than the OPE observed in the 2011 NASA

DISCOVER-AQ campaign in the Baltimore/Washington area. We will soon submit a more detailed paper discussing OPE in the Mid-Atlantic States in the future.

*Page 3148 line 16 To my eye the profile in Figure 7c is not uniform as it has a distinct bulge at 1 km.*

Response: We agree that the vertical distribution of afternoon ozone is not perfectly uniform, and that is why we state that “the mean ozone altitude profile shows a quasi-uniform concentration”. This assumption (the ozone in the lower troposphere is well mixed) can be used to estimate the decreasing trend of ozone near the surface in ppbv/year.

*Page 3148 line 5 The individual profiles in this figure are not visible at all.*

Response: We show the individual data points from all profiles, not the individual profiles. We have revised this sentence to read “... all aircraft measurements of tropospheric ozone obtained in summer 2001 are shown in Figure 7 ...”.

*Page 3149 line 18 Use baseline instead of background*

Response: We will follow this suggestion.

*Page 3150 first paragraph As you say, the RAMMPP profiles are from heavily polluted days while Figure 4 is for all pollution levels. So I don't see how you can specifically conclude anything about the role of transport.*

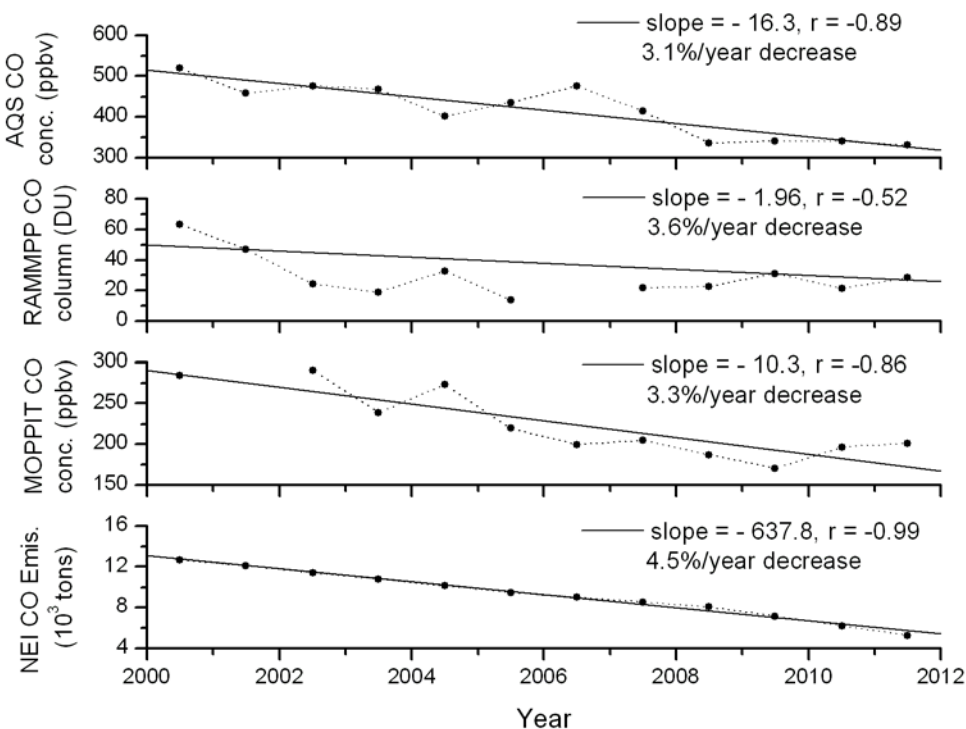
Response: The RAMMPP flights occurred when poor air quality, created by a combination of high temperatures and regional transport, was forecasted by MDE (please see the flight planning section on Page 3143). Thus these forecasts were based on the transport of air pollutants, and we knew the ozone measured would be influenced by both local pollutants and regional transport (westerly or southerly transport) of pollutants.

*Page 3150 line 20 Cooper et al 2012 show ozone trends of -1 ppbv per year across much of the Mid-Atlantic during summer when considering the 95th percentile of ozone values. These events should correspond to your RAMMPP profiles which occurred on highly polluted days. So according to Cooper et al, the rate of decrease for polluted events is 10 ppbv per decade, similar to your 13 ppbv per decade value.*

Response: We thank the reviewer for this comment, which supports our conclusion. We will add the results from Cooper et al. to the introduction. This paragraph will be revised to read “... The explanation of this difference could be that RAMMPP research flights were usually conducted on air quality action days, suggesting that for these conditions (i.e., meteorological conditions conducive to bad air quality), ozone pollution has improved more than for other times. Cooper et al. (2012) observed a ~15 ppbv decrease of surface ozone in the 95<sup>th</sup> percentile of the eastern U.S. summertime ozone from the early 1990's to the late 2000's. These results are consistent with the results from our long-term RAMMPP aircraft measurements ...”.

Page 3151 Here you compare the decrease in CO from the aircraft to the decrease at the surface based on the national average. You then go on to say why this is an apples and oranges comparison illustrating why this is the wrong approach. A much better approach is use the actual CO measurements from the surface monitors in your region and calculate the observed trend for your area during the summer months as shown in your Figure 3

Response: We follow this suggestion, and re-plot Figure 11 with AQS observations, RAMMPP measurements, MOPPITT products, and NEI emissions. The AQS surface observations show the same trend as the other three data sets.



Page 3153 Use the term “transport pathways” rather than circulation patterns.

Response: We will use ‘transport pathways’ in this manuscript.

Page 3153 The estimates of the emitted NO<sub>x</sub> associated with the trajectories uses as crude method that is not up to the standards of ACP. For example this method does not account for the altitude of the trajectories. What if the trajectory crosses an emission source but is above the boundary layer? In this case the trajectory won’t pick up any emissions. Furthermore no consideration is given to the speed of the trajectory, with a slower trajectory having a longer residence time and more time to accumulate emissions. The better method would be to use a chemical transport model, or to use inverse modeling, such as the FLEXPART retroplume method. This section should be deleted. The paper does not lose anything by dropping this section. The authors did not provide any description of the weather or transport conditions associated with each cluster. It would also be very useful to plot the typical observed trace gas

*mixing ratios associated with each cluster. Are pollution events more severe when the transport is from a particular direction? To my way of thinking this would be an appropriate and interesting use of the clusters.*

Response: Our clustering analysis, the hierarchical clustering technique described in Hains et al. (2008), does in fact consider the altitude and distance of each trajectory and includes information about the wind speed. Details, including concentrations for each cluster, are described in Hains et al. (2008). In this manuscript, we applied this approach, leaving details of the technique to Hains et al. (2008) paper. While chemical transport modeling and inverse modeling like FLEXPART are useful tools for studying air quality episodes, it is impractical to investigate the 15-year trend of air pollution in the Mid-Atlantic States with such models. The usage of these models is beyond the scope of this paper. We agree that the weather conditions are not described, but RAMMPP flights are only called on summer air quality action days with high temperature, low cloud cover, and no strong convective activity (e.g., T-storms, for safety concerns). The weather and transport conditions were similar on our flight days, as described in the flight planning section (Page 3143). We also discuss changing the coefficient of transport, which shows that the correlation between ozone columns and NO<sub>x</sub> emissions is not sensitive to the values of these coefficients. Our approach demonstrates that regional transport of ozone precursors from the Ohio River Valley plays an important role in air quality of downwind states, such as Maryland. These results are important for policy decision of the Mid-Atlantic states, where regional transport is important. As such, we feel it is important that they remain in this manuscript. Finally, we note that the other reviewer states that this is a major finding of this manuscript.

*Various pages There are many instances when mixing ratios are referred to as concentrations (for example Figure S5). This is incorrect and mixing ratios must be referred to as mixing ratios.*

Response: We follow this suggestion, and will use ‘mixing ratio’ in the revised manuscript.

*Figure 1 Please add labels to the map to indicate the locations of the 5 airports with the most profiles.*

Response: The location of these airports is revealed on Figure 1 as the place where the flight tracks spiral. We have revised the caption of Figure 1 to read “...Five airports (the spiral locations) extensively covered by this flight pattern are (from the lower left, clockwise) ...”.

*Figure 4 The regression line appears to be in error. The way it is drawn there are much stronger deviations below the line than above. I used the linear equation provided to check the endpoints and the y-values that I get for 1996 and 2012 are, 66.7 and 57.0, respectively. These numbers are 10 ppbv greater than even the values that are plotted. Please correct. Also, please make it clear that the ozone values are based on afternoon measurements.*

Response: The linear regression analysis shown is correct, however we need to add one more significant digit to the slope. Regardless, the usage of a line for the regression is misleading because the ozone will not increase to 1284.3 ppbv in 0 AD. Upon revision, we will only give the slope of the linear regression (in the same format of Figure 11) as illustrated below:



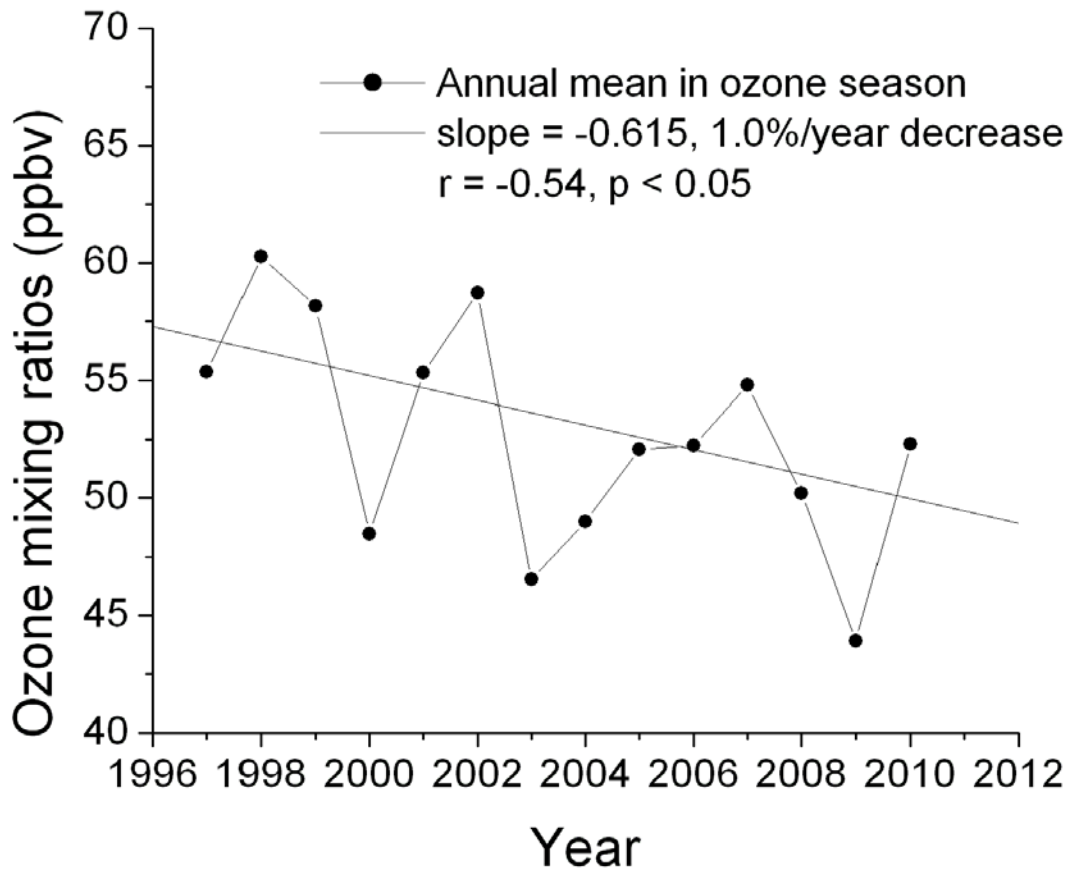


Figure 8 The mean value at 3 km is over 200 ppbv which seems high. How does this compare to the most recent year of data? Has there been a downward trend at 3 km? If so this would be an important result, showing that emissions changes at the surface have an effect as high as 3 km.

Response: The high CO (~200 ppbv) at 3 km was observed in 2001, more than ten years ago when the air pollution was much worse. In recent years, CO in the FT has decreased substantially. We agree that CO in the FT might not reflect local CO pollution, but might represent the CO pollution in upwind regions. Upon revision, we will cite Hallock-Waters et al. (1999), “Carbon monoxide in the U.S. mid-Atlantic troposphere: Evidence for a decreasing trend. *Geophysical Research Letters* 26: doi: 10.1029/1999GL900609. issn: 0094-8276”.

We can get an impression of the CO concentration trend in the upper levels of our profiles, with some important caveats. Due to flight pattern changes in the last 15 years, the ceiling of research spirals has been changed from 1.5 km in the late 1990’s to 2.5 km and 3.0 km in the 2000’s. We don’t have enough measurements to conduct a robust statistical analysis of CO mixing ratios at 3 km. For purpose of this response, we present an analysis of the CO mixing ratio between 1500 m and 2500 m. In summer, these altitudes are in the FT, well above the PBL. Based on the figure below, CO decreases from ~ 250 ppbv in the early 2000’s to ~150 ppbv in the early 2010’s within this altitude region. CO columns fall to their minimum value in 2004, which is likely due to the a very limited number of research flights in that year. Flight

sampling bias (discussed in section 3.3.3) also strongly influences the analysis of CO in the FT. In summary, we do not have solid enough evidence to make definitive statements about CO trends in the FT, so this discussion will not be incorporated into the revised manuscript.

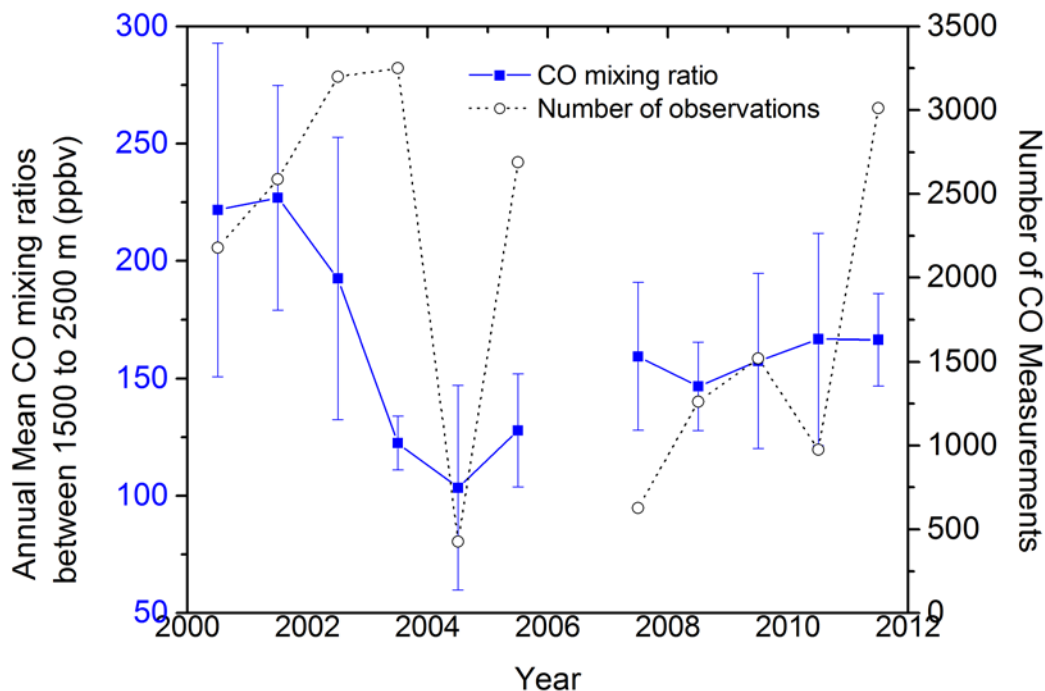


Figure S2 I don't understand why the Annual US emissions are scaled by 4% and 5%. What does "better demonstration" mean?

Response: The 'better demonstration' means that we use the scaled data from the national emissions, i.e., emissions from these states in the research domain, estimated from national data. We will rephrase this caption for better clarity.

Finally, we appreciate your comments on grammar, and we will polish the English in the final version.