Response to Reviewer's comments on He et al. ACPD 2013-11

We thank the reviewers for thoroughly reading our manuscript and providing helpful comments and suggestions, which will lead to a significant improvement of the manuscript. The detailed responses to major comments are listed below (text in italics shows comments from the reviewers, and the text in blue is our response):

SUMMARY & OVERALL RECOMMENDATION.
A paper of very high interest to the ACP community combining emissions inventories, some satellite data and aircraft profiles to conclude that large (50% or more) decreases in NOX and CO emissions in the Ohio/Penna region (mostly) with minor contribution from local source reductions have led to significant tropospheric ozone declines in the B/W region. The latter are given in terms of of 2/3 ozone production decrease (in ppbv ozone/day), column amount and absolute near-surface ozone loss (13 ppbv/decade). Take-home messages are (1) emission controls are effective in reducing ozone in the mid-Atlantic; (2) the losses in ozone are roughly consistent with reductions in reported CO and NOX emissions; (3) trajectory analyses coupled with B/W ozone losses suggest the reduction of NOX in the Ohio/Penna power-plant source region is primarily responsible for the ozone exceedance improvement that is observed over the 1997-2011 period. The analyses are conducted carefully and logically and presented with appropriate support, uncertainties and interpretation. The paper should be published after careful revision. It could be more tightly organized, some new studies (from 2011 DISCOVER-AQ, recently published or in press) should be cited to strengthen background and interpretation; minor corrections are needed for facts, grammar (see "Minor Points" below). The Abstract does not capture the above enumerated points as effectively as it could and should in order that the work carries full impact. The caveat, noted in the paper (see comment below about ozone decrease), that values reported here reflect the sampling bias of the aircraft (toward the most polluted summer conditions), should appear in the Abstract. Indeed, one aspect of confusion in the paper is use of annually averaged emissions amounts and some figures that appear to have continuous or full-year information, when the RAMMPP (page 3139) observations come from basically a summertime sampling/modeling project. The results appear to be internally consistent in this respect but the distinctions of summer vs annual need to come out in the Abstract. This could be a really high-impact paper!

Response: We appreciate the positive comments, and the manuscript will be revised according to these comments as discussed below.

SPECIFIC COMMENTS/RECOMMENDATIONS.
ABSTRACT. See general comments above to guide a revision. The CO and ozone reductions are described but analysis and text give ample space to NOX decreases since 2003 as a main driver for ozone improvements. NOX is not even mentioned in the Abstract! Likewise, text shows the importance of including the CPF in trends analysis and this is not mentioned either.

Response: We have re-written the abstract to represent the key conclusions of this study. The new abstract will read as:

"Trends in the composition of the lower atmosphere (0-1500 m altitude) and surface air quality over the Baltimore/Washington area and surrounding states were investigated for the period from 1997 to 2011. We examined observed and inventoried emissions, ground-level observations and long-term aircraft measurements to characterize trends in air pollution. The USEPA Continuous Emissions Monitoring System (CEMS) program reported substantial decreases in summertime nitrogen oxides (NO_x) emissions from point sources, up to ~80% in the Mid-Atlantic States, resulting from national and regional control measures. These large reductions in NO_x emissions are reflected in the ground-level observations with a sharp decrease around 2003. The decreasing trend of tropospheric CO columns observed by aircraft is ~8.0 Dobson Unit (DU) per decade (DU/decade), corresponding to ~350 ppbv/decade in the lower troposphere (the surface to 1500 m above ground level). Satellite observations of long-term, near-surface CO show ~40% decrease over the western Maryland between 2000 and 2011, the same magnitude as indicated by aircraft measurements above regions upwind of Baltimore/Washington airshed. With decreasing emissions of ozone precursors, the ground-level ozone in the Baltimore/Washington area showed a 6 ppbv/decade decrease in the last 15 years. Since photochemical production of ozone is substantially influenced by the ambient temperature, we introduce the climate penalty factor (CPF) into trend analysis of long-term aircraft measurements. After compensating for inter-annual temperature variations, historical aircraft measurements suggest the daily net production of tropospheric ozone over Baltimore/Washington area decreased from ~20 ppbv/day in the late 1990s to ~7 ppbv/day in the early 2010s during ozone season. A decrease in the long-term ozone column is observed as ~2.0 DU/decade in the lowest 1500 m, corresponding to ~13 ppbv/decade decrease. These aircraft measurements were conducted during days with severe ozone pollution forecasted, these results represent the decreasing trend in high ozone events over the last 15 years. Back trajectory cluster analysis demonstrates that emissions of air pollutants from Ohio and Pennsylvania through Maryland influence the column of downwind ozone in the lower atmosphere. The trends in air pollutants reveal the success of regulations implemented over the last decade and the importance of region wide emission controls over the eastern United States."

INTRODUCTION. This is somewhat disjointed. A lot of references are listed without mention of the main points relevant to the current study. In particular, a number of RAMMP-related studies are listed. The context from them would be useful to placing the current study in perspective. Which are most relevant? Which gave previous background on ozone, CO or NOX in the B/W region that relate to the current paper? Expand as appropriate. If other papers from the UMD group and beyond are less essential, omit them.

Response: We will re-organize the introduction to improve the flow, which we now see was indeed a bit disjoint. Originally, we had cited 11 RAMMPP-related papers in the Introduction. Upon revision, we will stream-line and cite only the most relevant RAMMPP-related papers: Taubman et al., (2006) and Hains et al., (2008).

Somewhat in contrast to the above request to trim, it is recommended to include recently published and (in press) papers from DISCOVER-AQ that are relevant to the current paper because (1) conditions like sea-breeze that affect part of the B/W domain are analyzed; (2) profile data from aircraft and sondes relevant to the RAMMPP studies are described and in some cases compared to satellite and groundbased
columns. Specific papers as follows: Martins et al., JGR, 2012 (on Hampton, VA sea-breeze); Martins et al, J Atmos Chem, 2013; Reed et al, J Atmos Chem, 2013; Stauffer et al., J Atmos Chem, 2012; Stauffer and Thompson, J Atmos Chem, 2013. D. K. Martins, R. M. Stauffer, A. M. Thompson, M. Pippin, T. Knepp, Surface ozone at a coastal suburban site in 2009 and 2010: Relationships to chemical and meteorological processes, J. Geophys. Res., 117, D05306, doi: 10.1029/2011JD016828, 2012. R. M. Stauffer, A. M. Thompson, D. K. Martins, R. D. Clark, C. P. Loughner, R. Delgado, T. A. Berkoff, E. C. Gluth, R. R. Dickerson, J. W. Stehr, M. A. Tzortziou, A. J. Weinheimer, Bay breeze influence on surface ozone at Edgewood, MD, during July 2011, J. Atmos. Chem., doi: 10.1007/s10874-012-9241-6, 2012 D. K. Martins, R. M. Stauffer, A. M. Thompson, H. S. Halliday, D. W. Kollonige, E. Joseph, A. J. Weinheimer, Ozone correlations between upper air partial columns and the near-surface at two mid-Atlantic sites during the DISCOVER-AQ campaign in July 2011, J. Atmos. Chem., revised in review, 2013. A. J. Reed, A. M. Thompson, D. E. Kollonige, D. K. Martins, M. A. Tzortziou, J. R. Herman, T. A. Berkoff, N. K. Abuhassan, A. Cede, Effects of local meteorology and aerosols on ozone and nitrogen dioxide retrievals from OMI and Pandora spectrometers in Maryland, USA during DISCOVER-AQ 2011, J. Atmos. Chem., in press, 2013. R. M. Stauffer and A. M. Thompson, Bay breeze climatology at two sites along the Chesapeake Bay from 1986-2010: Implications for surface ozone, J. Atmos. Chem., joch-12-0508, in press, 2013. A. M. Thompson, R. M. Stauffer, S. K. Miller, D. K. Martins, E. Joseph, A. J. Weinheimer, G. S. Diskin, Ozone profiles in the Baltimore-Washington region (2006-2011): Satellite comparisons and DISCOVER-AQ observations, J. Atmos. Chem., joch-13-0007, submitted, 2013.

Response: The recently conducted DISCOVER-AQ mission is indeed extremely important to understand air pollution in the mid-Atlantic region, nicely complementing the 15 year record of airborne measurements that are the basis of this manuscript. Upon revision, we will cite Martins et al, (2012), and Stauffer et al. (2013). We do not have access to the other four papers suggested by the reviewer, as these papers are either in press or still under review. We will track the status of these papers and, if they become available as our paper progress and if any indeed seem appropriate to reference, we will of course include citations in our final revised paper.

SECTION 2. Page 3141 lists a number of satellite instruments but some of these are not relevant to the current study. MOPITT is and SCIAMACHY trends in NOX may be. TES? IASI? AIRS? Incidentally, there is an error; AIRS is on Aqua not Aura (line 14).

Response: We had listed the other satellite instruments to indicate CO is a common measurement from space, and because they are used in Worden et al. (2012). However, we agree that this list is not all relevant to our study and upon revision we will remove the sentence:

"Tropospheric CO can been measured from satellites, such as Measurements of Pollution In The Troposphere (MOPITT) on Terra (Deeter et al., 2003), Atmospheric Infrared Sounder (AIRS) on

Aura (Warner et al., 2007), Tropospheric Emission Spectrometer (TES) on Aura (Luo et al., 2007), Infrared Atmospheric Sounding Interferometer (IASI) on METOP-A (George et al., 2009), and Scanning Imaging Absorption Spectrometer for Atmospheric Chartography (SCIAMACHY) on Envisat (Buchwitz et al., 2004)."

The sentence "Launched in 1999, MOPITT has proven useful for tracking the long-term trend of tropospheric CO on regional scales (Worden et al., 2012)."

Will be revised to:

" The MOPITT (Measurements of Pollution In The Troposphere) on Terra (Deeter et al., 2003), launched in 1999, has together with measurements from numerous other satellite instruments proven useful for tracking long-term trends in tropospheric CO on regional scales (Worden et al., 2013)."

Page 3141- Lines 24-28 - this is confusing - can you simply refer to the MOPITT version and characteristics in the data as used in the present study?

Response: The version of MOPITT data used here is relatively new, with a large variability in sensitivity to CO that must be accounted for in the analysis. This needs to be understood and described for any readers who might use this MOPITT data product for similar analyses. We will try to make this less confusing by revising these sentences as follows:

"Here we used the MOPITT version 5 level 3 monthly products that exploit both near and thermal infrared radiances (MOP03JM.005, http://eosweb.larc.nasa.gov/PRODOCS/mopitt/table_mopitt). We selected the CO values from the surface to 900 hPa (Deeter et al., 2012) to compare with RAMMPP aircraft measurements of CO in the lower troposphere. We note that although MOPITT multispectral retrievals have highly variable sensitivity to near-surface CO over different surface types, retrievals over the Mid-Atlantic region considered in this study showed consistently good sensitivity to near surface CO (Worden et al., 2010). For the MOPITT data used in this analysis, the sensitivity to CO typically peaks in the surface layer from 1000 hPa to 900 hPa and falls off exponentially with a scale height of ~1 km, making them suitable for comparison with our aircraft measurements."

Page 3142. Mentioned are 1000 flights along east coast but only a certain # in Balto/Wash area. Specify how many profiles used in the current analysis.

Response: We will add the number of vertical profiles used in this study including this new sentence: 'Here we examine ~500 research spirals over more than 20 airports in the Baltimore/Washington airshed.'

Page 3143. Although not as large in domain as the LLJ, sea breeze has a large impact at some B/W sites. At line 9, suggest revising to .. Two important transport processes in the mid-Atlantic region that affect summertime pollution are the low-level jet (LLJ) and sea-breeze. The LLJ (Corsemeier, etc) transports ozone and its precursors from the south. .... Due to the proximity of the Chesapeake Bay to Baltimore, sea breeze is significant in certain locations within the B/W

study region (Stauffer et al, 2012; Stauffer and Thompson, 2013; Thompson et al., 2013). Indeed, as emissions of ozone precursors and as shown below, ozone itself, decline significantly in the mid-Atlantic region, the presence of sea-breeze appears to play a decisive role in air quality exceedance episodes (cf Martins et al., 2012).

Response: We agree that the Chesapeake Bay breeze substantially influences summertime air quality in particular locals of the Baltimore/Washington area. However, this paragraph is focused on RAMMPP flight planning. RAMMPP flights conducted to date are planned in coordination with MDE on days with forecast levels of elevated surface ozone. The flight planning to date has emphasized sampling influx of ozone to the region via either westerly transport (from OH and PA) or southerly transport (from VA). The bay breeze affects surface conditions in the vicinity of Chesapeake Bay, as noted also in a paper from our group (Loughner et al., 2011). Sampling of effects of the Bay Breeze has not yet been incorporated into RAMMPP flight plans. As a result, we would like upon revision to keep the paragraph in question largely the same. However, the Martins et al., (2012) and the Stauffter et al. (2012) will be cited upon revision, elsewhere in the paper. If the other two papers note above are available for citation before our manuscript is finalized, we will consider adding citations to those as well.

MINOR POINTS (Sections 1-2) . Page 3138 Line 20 delete (and ozonesondes, etc) - Four years in Yorks et al is not "long-term" and extension of the B/W (Beltsville) record in Thompson et al (2013) is inconclusive (still only 8 years total).

Response: We follow this suggestion, and Yorks et al. will be cited, but not as in the context of 'long-term' record.

Page 3147 Lines 20-24. You mention "complicated" chemistry as responsible for a less than expected ozone reduction. How about the CPF? Is this the best place to mention or reference Bloomer et al for the first time [it appears on page 3149]?

Response: As suggested by the other reviewer, we will delete this paragraph from this manuscript. See details in our response to reviewer 2.

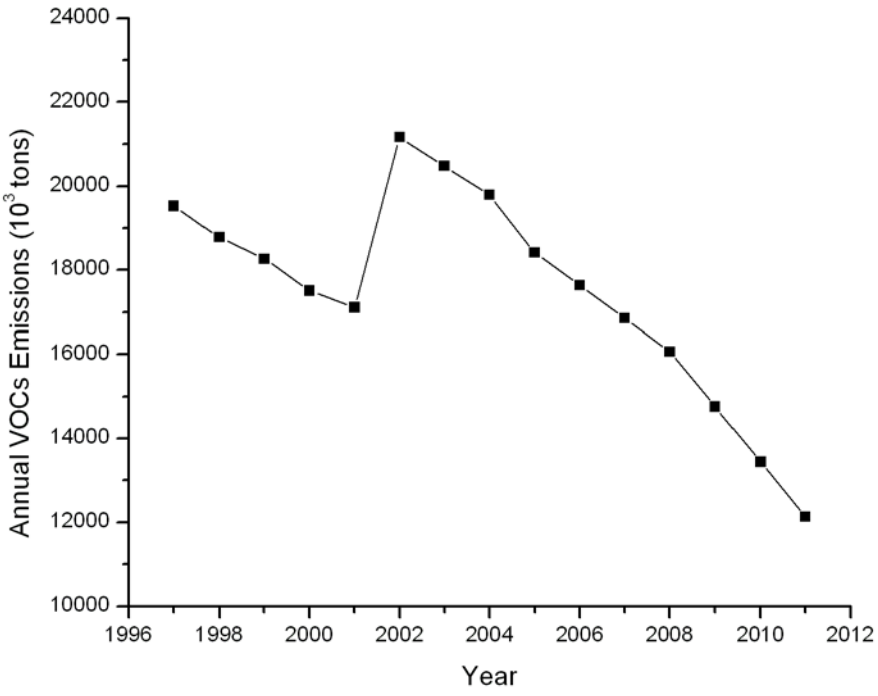
*Page 3150 Lines 18-24 - this is a major point of the paper, ie column ozone cleanup is greater than surface (!) But this figure might be biased by sampling conditions of flights. This key take-home message is *also* missing from Abstract.*

Response: We follow this suggestion, and will add the discussion on possible sampling bias of aircraft measurements to this manuscript. Also, this message will appear in the revised abstract.

Page 3152 Lines 15-18 The argument about magnitude of CO reduction makes sense but does this assume that VOC oxidation to CO is not a significant source in this biogenically rich area (given that mobile VOC emissions have also probably declined)?

Response: We agree the VOC oxidation to CO is an important source in the Baltimore/Washington area. For anthropogenic VOCs, national emissions decreased around ~40% (from ~2.0×10^7 tons/yr in 1997 to 1.2×10^7 tons/yr in 2011, see the figure below, the jump

between 2002 and 2003 is caused due to differences in emissions estimation methodologies, see http://cfpub.epa.gov/eroe/index.cfm?fuseaction=detail.viewInd&lv=list.listbyalpha&r=219697&subtop=341), which parallels the decreasing trend of CO emissions presented in Figure 11. During the summer in the Mid-Atlantic States, emissions of biogenic VOCs, especially isoprene, dominate CO pollution. We assume that the emissions of biogenic VOCs have not changed in the last 15 years. Therefore, in the manuscript, we only discuss the CO trends with respect to CO emissions in the Mid-Atlantic. We will add the discussion of VOC oxidation into the revised manuscript.



Lastly, we appreciate the various minor comments, most of which focused on grammar and details about presentation on the figures. All will be addressed, as suggested, upon revision..