Response to anonymous Referee #2

Summary:

This paper presents and analyzes a large data set that is a 10-year record of ozone and CO measurements at 7 sites in the northeast U.S. The authors have done a wide variety of analyses, described in long discussions, but in the end, they can draw no firm conclusions. The work as it stands has major shortcomings. I suggest that this paper be rejected. The following comments describe my concerns.

We would like to thank the reviewer for their comments on the article. We now defined "baseline" in the abstract and introduction explicitly and more clearly, reorganized figures and tables, and emphasized the quality control of measurement data that were used in the study. Detailed point-to-point response to the reviewer's comments was provided as follows.

Major issues:

1) The title of the paper emphasizes my first concern. The term "baseline" concentration has a specific meaning, which I believe was originally defined in the 2009 HTAP Report entitled "Hemispheric Transport Of Air Pollution 2010:

> "A baseline concentration is an observation made at a site when it is not influenced by recent, locally emitted or produced pollution. These baseline sites are typically situated in locations with minimal and infrequent impact from local sources of anthropogenic pollution. Observations may be made continuously and subsequently sorted, or air samples taken only when meteorological conditions are such that the recorded concentrations are free from the local contamination. Time series of baseline concentrations provide the range and frequency of pollutant concentrations transported to the site from upwind locations. However the requirement that only recently emitted or produced local pollution be excluded means that baseline concentrations may contain traces of local pollutants that were emitted many days earlier and became well-mixed with other air masses. There is no strict definition of "recently" emitted or produced local sources of anthropogenic pollution."

The current paper selects data to analyze that is labeled "baseline" but in fact no means was identified to determine the influence of "locally emitted or produced pollution". I do not believe that it is possible to determine baseline concentrations of CO or ozone at any site in the northeastern US, since the region is surrounded by pollutant sources, and most of the North American continent lies upwind of that region. Furthermore, characterization of baseline concentrations requires defining the distribution of concentrations that are measured under baseline conditions. They may be low concentrations, but they may also be high concentrations. For example, baseline concentrations of CO may be elevated if anthropogenic emissions or wildfire emissions are transported to the site from a distant continent, and baseline

concentrations of ozone may be greatly elevated if a stratospheric intrusion is transported to the site.

It is the reviewer's opinion that it is impossible to determine baseline concentrations of CO or O_3 at any site in the northeastern US. We disagree with that. In a multi-year time series of CO, the baseline is simply the line that consists of the lowest values of certain time intervals, be daily or monthly. An example is shown in Figure S2. We gave this baseline a range by using monthly 10^{th} percentile values. There is no policy connotation intended in the term "baseline" used in this study.

There is clearly a lack of a universal definition of baseline CO or O_3 in the scientific community. The 2009 HTAP report was a great effort to present the consensus of such definitions from the community's decades of research. During the past three decades, a great number of studies have investigated the trends and variability in background or baseline O_3 (e.g., Altshuller, 1987; Altshuller and Lefohn, 1996; Cooper et al., 2010; Cui et al., 2011; Derwent et al., 2007; Jaffe et al., 2003; Lin et al., 2000; Logan et al., 2012; Parrish et al., 2009; Wilson et al., 2012). Background and baseline are used, often interchangeably, to quantify how much O_3 produced from recent or local anthropogenic emissions could be allowed to attain the O_3 standards (HTAP, 2010; Huang et al., 2015). A few recent studies discussed the difference between background O_3 and baseline O_3 (Chan and Vet, 2010; HTAP, 2010; Huang et al., 2015; Parrish et al., 2012). The term "background" was used in modeling studies that estimated the atmospheric mixing ratio of a compound determined by natural sources only (HTAP, 2010; Chan et al., 2010; Parrish et al., 2012; Huang et al., 2015). Parrish et al. (2010) pointed out that the US Environmental Protection Agency (EPA) used a similar term, Policy Relevant Background (PRB), which was defined as O_3 that would exist in the absence of North American anthropogenic emissions. Fiore et al., (2002) defined background O_3 as O_3 produced outside the North American boundary layer (surface to 700 hPa) and naturally formed O_3 within the U.S., using a three-dimensional global tropospheric chemistry model (GEOS-Chem). Huang et al. (2015) estimated western U.S. background O_3 by zeroing out the U.S. anthropogenic emissions in the regional Sulfur Transport and dEposition Model (STEM). However, it is impossible to quantify this type of background O_3 using observational data, as the effect of North American emissions is inherently included in ambient measurements (Chan et al., 2010; Parrish et al., 2010).

The term "baseline" referred to concentration levels of compounds at times when fresh/local emission influences were negligible and can be obtained from measurement records by removing data of local influences (HTAP, 2010; Chan et al., 2010; Parrish et al., 2012; Huang et al., 2015). Various methods have been utilized to diagnose baseline conditions, including measurements at remote sites, analysis of the probability distribution of pollutants, and correlations with reactive nitrogen oxides (e.g. Altshuller and Lefohn, 1996; Lin et al., 2000; Jaffe et al., 2003; Derwent et al., 2007; Parrish et al., 2009; Cui et al., 2011; Wilson et al., 2012). Here are a few examples using measurement data from remote sites or rural sites, which are in geographic approximation from urban/industrial source regions that are similar to our sites. Lin et al. (2000) analyzed the

probability distribution of O_3 concentrations at U.S. rural sites over 1980 – 1998 and defined baseline O_3 concentrations as the median values for the lowest 25th percentiles of CO and NO_y concentrations. Jaffe et al. (2003) extracted baseline data from the total dataset by selecting time periods of high winds from the direction of the Pacific coast and isentropic back-trajectories that has not in contact with the continent for more than 24 hours. Derwent et al. (2007) used halocarbons and CO to identify polluted air masses at Mace Head and used the NAME Lagrangian dispersion model to exclude times when air masses were from east of Mace Head or southern latitudes, or when the air was not well mixed around the station. Parrish et al. (2009) selected baseline conditions when samples were collected during a high, onshore local wind window. Cui et al. (2011) selected baseline conditions at Jungfraujoch by running 20-day back trajectories and air masses without contact with the European boundary layer were considered baseline periods. Wilson et al. (2012) used the 5th percentile value of O_3 mixing ratios as a measure of the baseline or background conditions.

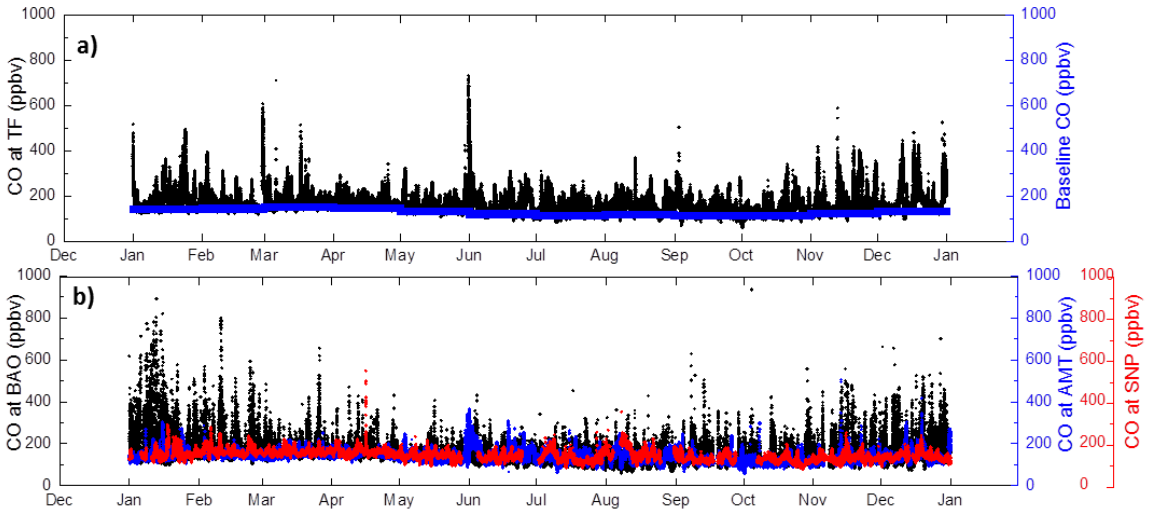

Figure S2 (a). Time series of 1-min CO (ppbv) and monthly baseline CO (ppbv) at TF in 2010. (b) Time series of 5- min CO (ppbv) at BAO, AMT, and SNP in 2010.

In our study, all the seven sites are located in rural areas of the Northeast U.S. They are ~100 km far away from the Northeast urban corridor and at least ~200 km away from the Ohio River Valley, the major industrial region in the Northeast US. We estimated the baseline CO and baseline O_3 using criteria similar to that from Lin et al. (2000), Mao et al. (2008), Mao and Talbot, (2012). Baseline CO was determined using the monthly 10th percentile level of CO at low elevation rural sites and 50th percentile at the two mountain sites. Monthly median O_3 levels of the baseline air were defined as baseline O_3 levels. We only used the data during daytime when the convective boundary layer is fully developed and measurements at a surface site was more regionally representative. Specifically, Figure S2 shows time series of 1-min CO and monthly baseline CO at TF in 2010. Monthly baseline CO quantified by our method was able to track the variation of the low level CO mixing ratios at this site (Figure S2a). Using the dataset from the NOAA Earth System Research Laboratory Global Monitoring Division, we found annual

averaged CO was 138 ppbv at Argyle, Maine (AMT), 140 ppbv at Boulder, Colorado (BAO), and 148 ppbv at Shenandoah National Park, Virginia (SNP) (Figure S2b). Seasonal cycles at these three sites were similar to those found at TF, which had the maximum value of 150 ppbv in March and the minimum value of 111 ppbv in September. As demonstrated in Section 3.3.1, baseline CO mixing ratios over our study region were significantly impacted by wildfires in Russia and Canada. Specifically, owing to expansive wildfires in Siberia, baseline CO in summer 2003 was 130 ppbv at AI, 171 ppbv at MWO, 148 ppbv at TF, 187 ppbv at PSP, and 183 ppbv at WFM, where were much higher than in normal years.

Baseline O_3 mixing ratios from our study ranged from 28 – 56 ppbv over 2001 – 2010, which were consistent with values of US continental background O_3 (35±10 ppbv in summer and 45±10 ppbv in early spring) estimated using various techniques in other studies (Altshuller and Lefohn, 1996; Lin et al., 2000; Jaffe et al., 2003; Parrish et al., 2009; Chan et al., 2010). Although baseline O_3 was obtained by correlation with low mixing ratios of CO, baseline O_3 quantified by our method could be still influenced by stratospheric intrusion. Stratospheric air masses contain high mixing ratios of O_3 and very low mixing ratios of CO (Schroeder et al., 2014). Thus stratospheric intrusion can lead to dilution of surface CO and decrease CO levels, which were most likely captured by the monthly 10^{th} percentile criteria.

To reflect the investigative work in this study, the title was changed to "Regional and Hemispheric Influences on Variability and Trends of Baseline Carbon Monoxide and Ozone over the Northeast US".

At the beginning of the abstract, we added the definition of baseline CO and O_3: "Baseline carbon monoxide (CO) and ozone (O_3) were defined as mixing ratios of CO and O_3 under minimal influence of recent and local emissions. In this study, baseline carbon monoxide (CO) and ozone (O_3) were examined at seven rural sites in the Northeast US during varying periods over 2001–2010. Specifically, baseline air was determined using the monthly 10^{th} percentile level of CO at Appledore Island (AI), Castle Spring (CS), Pack Monadnock (PM), Thompson Farm (TF), Pinnacle State Park (PSP), and 50^{th} percentile level at Mt. Washington (MWO) and Whiteface Mountain (WFM). Monthly median O_3 levels of the baseline air were defined as baseline O_3 levels." (L28 – L35)

To clarify the definition of baseline, we added the following sentences in the Introduction:

"Background or baseline has been used, often interchangeably, to quantify how much O_3 produced from recent or local anthropogenic emissions could be allowed to attain the O_3 standards (HTAP, 2010; Huang et al., 2015). A few recent studies discussed the difference between background O_3 and baseline O_3 (HTAP, 2010; Huang et al., 2015; Parrish et al., 2012; Chan et al., 2010). The term "background" was used in modeling studies that estimated the atmospheric mixing ratio of a compound determined by natural sources only, while the term

"baseline" was obtained from measurement records by removing data of local influences (HTAP, 2010, Chan et al., 2010; Parrish et al., 2012)." (L108 – L115)

"Various methods have been utilized to diagnose baseline conditions, including using measurements at remote sites, analysis of the probability distribution of pollutants, correlations with reactive nitrogen oxides, and isentropic back-trajectories (e.g., Altshuller and Lefohn, 1996; Lin et al., 2000; Jaffe et al., 2003; Derwent et al., 2007; Parrish et al., 2009; Cui et al., 2011; Wilson et al., 2012)." (L117 – L121)

2) What the authors attempt to do in this paper is to determine monthly average concentrations of an approximate regional background of CO and O_3. It may be that a useful paper could be written discussing such background concentrations, and how they vary with the many variables that the authors consider. However, even such an analysis is compromised because the authors are not successful in describing a regional background that is actually regional. This is clear from Figure 2 where time series of the results are plotted. The background concentrations of CO and ozone determined for each of the seven sites are not the same. There are certainly similarities, but there are also large, unexplained differences. In my view, the authors must reconsider their analysis to arrive at two time series: one a monthly average regional background CO concentration, and the other a monthly average regional background ozone concentration. It is not clear to me that this can be achieved, but in Figure 2 there appears to be enough similarity between sites that it may be possible to derive time series that represent a regional background for the northeastern US.

The baseline CO and O_3 were defined as CO and O_3 measured at surface sites without the influence of strong local effects. Therefore, baseline CO and baseline O_3 could be impacted by local natural precursor emissions, distant natural emissions, distant anthropogenic emissions, downwind transport processes, photochemical conditions, and terrain conditions including deposition with respect to forest or agricultural areas (Altshuller and Lefohn 1996; Chan et al., 2010; HTAP, 2010). Baseline O_3 can also be influenced by stratospheric intrusion (e.g., Altshuller and Lefohn 1996; Schroeder et al., 2014). Thus, it was expected that baseline CO and O_3 would not be identical between the seven sites due to the varying meteorology, terrain, elevation (18 – 2100 m asl), and land surface (marine to mountain top) at the sites. MWO and WFM are the two highest sites situated close to the top of the daytime convective boundary layer and they are likely more impacted by long-range transport and stratospheric intrusion. PSP is located either on the periphery of the subtropical high in summer – fall, or the periphery of the North American trough (Figure. 5b–e). Thus, PSP could be less influenced by the westerly wind. TF, which is close to the northeast urban corridor, could be more influenced by downwind transport from urban areas.

We explicitly discussed differences of baseline CO and O_3 among each site in Sections 3.2 – 3.3. Those differences among each site also help to identify the impact of increasing Asian emissions, NOx emissions from the northeast urban corridor, and stratospheric intrusion over the Northeast

US. In addition, similarities and differences of baseline CO and O_3 derived from our study illustrated the range of baseline CO and O_3 over the Northeast US.

To better compare similarities and differences between the seven sites, we reorganized the time series in Figure 2 by separating the time series at the two mountainous sites MWO and WFM, from the other five lower elevation sites.

3) It is clear that there are experimental problems in the data set. In the discussion the authors note unexplained differences between results at different sites. Some of these are certainly due to experimental problems. Before, proceeding with any attempt to define a regional concentration, the authors must undertake a critical evaluation of their data sets to eliminate confounding experimental problems.

It is not clear to us what exactly those "unexplained differences" the reviewer referred to. As we stated in our response to the reviewer's Comment #2, we devoted Sections 3.2 – 3.3 to understanding the differences in baseline CO and O_3 between the sites. One unexplained difference we readily acknowledge is the unusually high CO mixing ratios at CS over May 2003 – June 2008. However, no evidence shows the causes for these high mixing ratios and suggests any experimental errors. We removed all the statements involving baseline CO at CS, and none of the conclusions was drawn based on this dataset. All other differences between sites were investigated and attributed to meaningful processes.

The data at five sites were obtained from the University of New Hampshire's AIRMAP Observing Network (http://www.eos.unh.edu/observatories/data.shtml), a NOAA funded regional climate and air quality program. Since 1999, the AIRMAP program has conducted a wide range of measurements of chemical species, including O_3, NO, NO_y, CO, CO_2, SO_2, elemental mercury (Hg°), reactive gaseous mercury (RGM), particle-bound mercury (HgP), hydrocarbons, halocarbons, and oxygenated compounds. All of these measurements have undergone rigorous quality control, and many papers using these datasets have been published in peer reviewed journals over the years. The publications covered various topics, such as synoptic controls on Northeast surface O_3, complex cycling of atmospheric mercury in terrestrial and coastal marine environments, and the distribution of hydrocarbons and halocarbons along coastal New England (e.g., Feddersen et al., 2012; Fischer and Talbot, 2005; Hegarty et al., 2007; Lai et al., 2012; Lombard et al., 2011; Mao et al., 2008; Mao and Talbot, 2004a, 2004b, 2004c, 2012; Sigler et al., 2009a, 2009b; Talbot et al., 2005, 2011). Specifically, CO was measured with Thermo Environmental Instruments model 48CTL. As the instrument baseline drifts constantly, it was operated in a mode where ambient air was monitored for 10 min followed by a 5-min zeroing interval. Zeroing was generating by converting CO to CO_2 using a hot (250 °C) palladium catalyst. Calibration was performed every 6.25 hours and it was conducted by providing a spike of 300 ppbv, which was dynamically diluted from ~5 ppmv (NIST traceable ±2%) CO standard from Scott Marrin, Inc. (Mao and Talbot, 2004). O_3 was measured using a Thermo Environmental Instruments model 49C-PS. The detection limit of the instrument was 1.0

ppbv. Instrument zeroing and calibration was achieved routinely by utilizing zeroing air and an internal primary O3 source, respectively. In addition, TF was a part of AMNet over January 1, 2009 – November 29, 2011.

The dataset at WFM and PSP were obtained from the State University of New York at Albany. The Atmospheric Sciences Research Center at University at Albany (ASRC), in collaboration with New York State Department of Environmental Conservation (NYSDEC), has maintained and operated these measurement sites for decades. All the data have been quality controlled with the strictest protocols. The ASRC supersite dataset has been used for numerous peer-reviewed publications over the past decade. They have been used to evaluate air quality models, characterize the process leading to the formation of ozone and $PM_{2.5}$, evaluate the regional impact of wildfires (e.g., Bae et al., 2011; Cai et al., 2008; Ren et al., 2003, 2006; Schwab et al., 2009).

We added a concise description including such information in the text (L214).

The correlations related to baseline CO at CS were deleted in Table 3 and Table 4. The statement "CS was not included, as mixing ratios of baseline CO at this site were unusually high over May 2003 – June 2008." was added in Table 3 and Table 4. "CS," was deleted in L570.

4) Pages 27263-27280 give an extended discussion of many topics. Much of this discussion is speculation regarding causes of trends, variability and correlation perceived in the data. For a useful paper to eventually arise from the authors' analysis, the speculation must be removed, and clear, well-reasoned discussion must be substituted. I suggest that the authors focus on a limited set of hypotheses that they feel they can discuss in a rigorous and complete manner.

The analysis on pages 27263-27280 resulted in the following findings:

1. Baseline CO at most sites decreased significantly at a rate between −4.3 to −2.3 ppbv yr^{-1}, while baseline O_3 was relatively constant;
2. Springtime and wintertime baseline CO at MWO and WFM did not exhibit a significant trend, possibly a result of the combined effect of decreasing emissions in the northeast US and increasing emissions in Asia;
3. Increasing springtime and wintertime baseline O_3 at TF was most likely caused by the decrease in NOx emissions over the urban corridor;
4. Summertime baseline CO and O_3 were predominantly influenced by biomass burning emissions and cyclone activities, which were related to the AO;
5. Negative correlation was found between baseline O_3 and the NAO index, potentially due to variations of solar flux, stratospheric intrusion, and continental export.

To arrive at each finding, we used detail-oriented quantitative analysis, logical discussion of our own results, and the findings from the literature. A case in point is Finding #3, for which we initially had four hypotheses, and after carefully examining the dataset of potential vorticity, the difference among sites with different elevation, and O_3 photochemistry in combination with

findings from previous studies (e.g., Cooper et al., 2012; Reidmiller et al., 2009; Wilson et al., 2012), we arrived at the point that decreasing NOx emissions over the northeast urban corridor was the most probable factor contributing to increasing wintertime and springtime baseline O_3 at TF.

Minor issues:

1) Figure 2 is confusing. The station labels in the annotations are not in accord with the figure caption. It is not clear which curve corresponds to which station.

Thanks for pointing out the mistake. Originally, Figures 2b and 2d showed time series of baseline CO and O_3 at WFM and PSP. We reorganized Figure 2, and in the new figure time series of baseline CO and O_3 at MWO and WFM were shown in Figure 2b and 2d.

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Regional and Hemispheric Influences on Variability and Trends of Baseline Carbon Monoxide and Ozone over the Northeast US~~Baseline carbon monoxide and ozone in the northeast US over 2001–2010~~

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Abstract

Baseline carbon monoxide (CO) and ozone (O_3) were defined as mixing ratios of CO and O_3 under minimal influence of recent and local emissions. In this study, ~~Baseline~~ baseline carbon monoxide (CO) and ozone (O_3) were examined~~studied~~ at seven rural sites in the northeast US during varying periods over 2001–2010. Specifically, baseline air was determined using the monthly 10^{th} percentile level of CO at Appledore Island (AI), Castle Spring (CS), Pack Monadnock (PM), Thompson Farm (TF), Pinnacle State Park (PSP), and 50^{th} percentile level at Mt. Washington (MWO) and Whiteface Mountain (WFM). Monthly median O_3 levels of the baseline air were defined as baseline O_3 levels. Interannual and seasonal variations of baseline CO and O_3 were examined for the effects of changes in anthropogenic emissions, stratospheric intrusion, transport pathways and O_3 photochemistry. Baseline CO generally exhibited decreasing trends at most sites, except at ~~Castle Spring (~~CS~~)~~, an elevated (~ 400 ma.s.l.) site in rural central New Hampshire. Over April 2001–December 2010, baseline CO at ~~Thompson Farm (~~TF~~)~~, ~~Pinnacle State Park (~~PSP~~)~~, and ~~Whiteface Mountain (~~WFM~~)~~ decreased at rates ranging from −4.3 to −2.5 ppbv yr^{-1}. Baseline CO decreased significantly at a rate of −2.3 ppbv yr^{-1} at ~~Mt. Washington (~~MWO~~)~~ over April 2001–March 2009, and −3.5 ppbv yr^{-1} at ~~Pack Monadnock (~~PM~~)~~ over July 2004–October 2010. Unlike baseline CO, baseline O_3 did not display a significant long term trend at any of the sites, resulting probably from opposite trends in NO_x emissions worldwide and possibly from the overall relatively constant mixing ratios of CH_4 in the 2000s. In looking into long term trends by season, wintertime baseline CO at MWO and WFM, the highest sites, did not exhibit a significant trend, probably due to the competing effects of decreasing CO emissions in the US and increasing emissions in Asia. Springtime and wintertime baseline O_3 at TF increased significantly at a rate of 2.4 and 2.7 ppbv yr^{-1},

respectively, which was likely linked to nitrogen oxides (NO_x) emissions reductions over urban areas and possible resultant increases in O_3 due to less titration by NO in urban plumes. The effects of meteorology on baseline O_3 and CO were investigated. A negative correlation was found between springtime baseline O_3 and the North Atlantic oscillation (NAO) index. It was found that during positive NAO years, lower baseline O_3 in the northeast US was linked to less solar radiation flux, weakened stratospheric intrusion, and intensified continental export. The lowest baseline CO at ~~Appledore Island (~~AI~~)~~, PM, TF, PSP, WFM and the lowest baseline O_3 at AI, PM, and PSP in summer 2009 were linked to the negative phase of the Arctic oscillation (AO), when more frequent cyclone activities brought more clean Arctic air to midlatitudes. It was also found that forest fires played a major role in determining baseline CO in the northeast US over 2001–2010. In summer, ~ 38 % of baseline CO variability at AI, CS, MWO, TF, PSP, and WFM could be explained by CO emissions from forest fires in Russia and ~ 22 % by emissions from forest fires in Canada. Long-range transport of O_3 and its precursors from biomass burning contributed to the highest baseline O_3 in summer 2003 at AI, CS, MWO, TF, and WFM. The findings of this study suggested impacts of increasing Asian emissions, NO_x emissions from the Northeast Urban corridor, global biomass burning emissions, and meteorological conditions (e.g. cyclone activity, AO, and NAO) should all be considered when designing strategies for meeting and maintaining National Ambient Air Quality Standards (NAAQS) and evaluating the air quality in the northeast US.

1 Introduction

Carbon monoxide (CO)~~O~~ is a product of incomplete combustion (e.g. fossil fuel, biofuel, and biomass burning) and oxidation of hydrocarbon compounds (Worden et al., 2013). CO is a major sink of hydroxyl radicals (OH), and hence changes in CO can impact many chemically important trace species that are removed via oxidation by OH (Daniel and Solomon, 1998; Petrenko et al., 2013). In the presence of nitrogen oxides (NO_x), CO oxidation is important in the tropospheric ozone (O_3) budget. Due to its relatively unreactive chemical nature, CO has been used as a tracer of anthropogenic influence and fire emissions (Gratz et al., 2014; Price et al., 2004; Weiss-Penzias et al., 2006).

Tropospheric ~~ozone (~~O_3~~)~~, which is produced largely by photochemical oxidation of ~~nitrogen oxides (~~NO_x~~)~~ and volatile organic compounds (VOCs), is a serious and ubiquitous air pollutant affecting humans' respiratory system, reducing yields of agricultural crops, and damaging natural ecosystems (EPA, 2012). As a precursor of ~~hydroxyl radicals (~~OH~~)~~, a dominant oxidant, O_3 regulates the atmospheric capacity of oxidation (Prinn, 2003). Tropospheric O_3 is also the third strongest greenhouse gas, after carbon dioxide (CO_2) and methane (CH_4), suggested by the Intergovernmental Panel on Climate Change (IPCC, 2007).

~~CO is a product of incomplete combustion (e.g. fossil fuel, biofuel, and biomass burning) and oxidation of hydrocarbon compounds (Worden et al., 2013). CO is a major sink of OH, and hence changes in CO can impact many chemically important trace species that are removed via oxidation by OH (Daniel and Solomon, 1998; Petrenko et al., 2013). In the presence of NO_x, CO oxidation is important in the tropospheric O_3 budget. Due to its relatively unreactive chemical nature, CO has been used as a tracer of anthropogenic influence and fire emissions (Gratz et al., 2014; Price et al., 2004; Weiss-Penzias et al., 2006).~~

The United States has made enormous efforts to control ambient mixing ratios of criteria pollutants since the 1970s (EPA, 2012). Nationally, annual second maximum 8 h average mixing ratios of CO decreased by 52 %, and annual mean mixing ratios of nitrogen dioxide (NO_2) declined by 33 % over 2001–2010 (EPA, 2012). Ambient O_3 concentrations in metropolitan areas, such as Los Angeles, New York City, and Chicago, decreased significantly in the past two decades (Bell et al., 2007; Cooper et al., 2010, 2012; Lefohn et al., 2010; Parrish et al., 2011). Despite the decreasing anthropogenic emissions in Europe and North America, emissions in China and India have increased. Biomass burning emissions vary both spatially and temporally (Granier et al., 2011; Gratz et al., 2014). It remains unclear how such opposing changes in emissions have globally affected baseline CO and O_3, which are defined as mixing ratios of CO and O_3 under minimal influence of recent and local emissions (Chan and Vet, 2010; HTAP, 2010).

Background or baseline has been used, often interchangeably, to quantify how much O_3 produced from recent or local anthropogenic emissions could be allowed to attain the O_3 standards (HTAP, 2010; Huang et al., 2015). A few recent studies discussed the difference between background O_3 and baseline O_3 (HTAP, 2010; Huang et al., 2015; Parrish et al., 2012; Chan et al., 2010). The term "background" was used in modeling studies that estimated the atmospheric mixing ratio of a compound determined by natural sources only, while the term "baseline" was obtained from measurement records by removing data of local influences (HTAP, 2010, Chan et al., 2010; Parrish et al., 2012). Quantitative estimates of baseline CO and O_3 are not straightforward since measurements at a particular location include contributions from local anthropogenic precursor emissions (Chan and Vet, 2010). Various methods have been utilized to diagnose baseline conditions, including using measurements at remote sites, analysis of the

probability distribution of pollutants, correlations with reactive nitrogen oxides, and isentropic back-trajectories (e.g., Altshuller and Lefohn, 1996; Lin et al., 2000; Jaffe et al., 2003; Derwent et al., 2007; Parrish et al., 2009; Cui et al., 2011; Wilson et al., 2012). ~~In the literature,~~ A~~a~~ir masses with low percentile values (< 20th percentile in the literature) of CO, an excellent anthropogenic tracer for its origin of mobile combustion, are commonly considered ~~background~~ baseline air (e.g., Lin et al., 2000; Mao and Talbot, 2012). Based on Lin et al. (2000), t~~T~~he low percentile value of CO is used as baseline CO, and baseline O_3 is then estimated using the data corresponding to CO mixing ratios below the baseline CO level ~~(e.g., Lin et al., 2000; Mao and Talbot, 2012)~~.

The lifetime of CO and O_3 in the free troposphere is ~ 2 months and ~ 20 days, respectively (Price et al., 2004; Stevenson et al., 2006). Thus, CO, O_3, and other precursors emitted in the upwind region and those produced in transit could affect the baseline CO and O_3 levels there~~be transported downwind and subsequently affect the baseline CO and O_3 levels there~~ (Cooper et al., 2012; Oltmans et al., 2008; Pollack et al., 2013). This has important regulatory implications, because the levels of baseline CO and O_3 directly affect emission control of CO and other O_3 precursors. Therefore, quantifying trends and variations in baseline CO and O_3 is of vital importance to assessing air quality and designing cost-effective emission control plans to meet the National Ambient Air Quality Standards (NAAQS) (http://www3.epa.gov/ttn/naaqs/criteria.html).

Studies have been conducted to investigate trends in baseline CO and O_3 across northern hemispheric mid-latitude~~s~~ regions, such as North America, Europe, and Asia, and no consistent trends have been found (Chan, 2009; Cooper et al., 2010; Cui et al., 2011; Logan et al., 2012; Oltmans et al., 2013; Parrish et al., 2012; Tilmes et al., 2012; Wilson et al., 2012; Xu et al.,

2008). ~~No consistent trends have been found.~~ Kumar et al. (2013) reported trends of −0.31 and −0.21 ppbv yr^{-1} for CO and O_3, respectively, at the Pico Mountain Observatory over 2001–2011. Gratz et al. (2014) reported that the springtime median mixing ratio of O_3 increased at a rate of 0.76 ppbv yr^{-1} at the Mt. Bachelor Observatory over 2004–2013, while median CO decreased at a rate of −3.1 ppbv yr^{-1}. Chan and Vet (2010) found that baseline O_3 in the eastern US decreased in spring, summer, and fall over 1997–2006, and the decadal trends in the Atlantic coastal region were positive in winter, summer, and fall. For the most part, causes for temporal variability have not been adequately explained. Interpretation of long-term trends is difficult because of significant interannual variability in emissions and climate as well as possibly in photochemistry (Hess and Lamarque, 2007). Climate change may lead to changes in natural emissions (e.g., emissions from wildfires, vegetation, and lightning), pollution transport pathways, and stratosphere-tropospheric exchange (Parrish et al., 2013).

Wildfires release large quantities of O_3 precursors, e.g., CO, VOCs, and NOx, every year. For instance, the MACCity emission inventory over 2001–2010 suggested that total global biomass burning emissions of CO ranged from ~ 300 to ~ 460 Tg yr^{-1}, close to ~ 590 Tg yr^{-1} anthropogenic emissions (Granier et al., 2011). These chemical species could make a significant contribution to tropospheric CO and O_3 budgets, impacting the interannual variability of surface CO and O_3 globally (Dutkiewicz et al., 2011; Herron-Thorpe et al., 2014; Honrath et al., 2004; Kang et al., 2014; Wigder et al., 2013; Wotawa and Trainer, 2000). Most studies focused on episodic enhancements in ~~demonstrated elevated~~ CO and O_3 linked to~~due to~~ fire emissions studies (e.g., DeBell et al., 2004; Dutkiewicz et al., 2011; Honrath et al., 2004)~~for an episode (Dutkiewicz et al., 2011; Honrath et al., 2004)~~. To the best of our knowledge, only two studies (Jaffe et al., 2004; Wotawa et al., 2001) examined~~quantified~~ the impact of wildfires on baseline

CO and O_3 over time periods of ten years in the 1990s ~~using ten-year observations~~. Thus m~~M~~ore research is warranted to determine the impact of wildfires on baseline CO and O3 in the 2000s in northern hemispheric midlatitudes.

Regional climatic processes over the US east coast are influenced by the North Atlantic Oscillation (NAO) and the Arctic Oscillation (AO) (Archambault et al., 2008; Hess and Lamarque, 2007). Studies suggested a link between NAO and regional distributions of tropospheric trace gases over the northwestern Atlantic Ocean, northern Europe, and the Arctic region based on model simulations or measurements (Christoudias et al., 2012; Creilson et al., 2003; Duncan and Bey, 2004; Eckhardt et al., 2003; Hegarty et al., 2009; Krichak and Alpert, 2005; Li et al., 2002; Pausata et al., 2012; Woollings and Blackburn, 2012). Most studies suggested that trace gases over North America could be transported across the Atlantic Ocean to northern Europe during the high NAO phase, particularly in winter and spring. However, to the best of our knowledge, nearly no studies examined the relationship between NAO and trace gases over the northeast US over 2001 – 2010. Circulation patterns can not only impact the transport of pollutants to the targeted region but can also influence the export from the upwind region. Hence, upwind trace gases are also likely to change in response to varying intensity of NAO.

The AO is another dominant mode of meteorological variability in the Northern Hemisphere (Creilson et al., 2005; Hess and Lamarque, 2007; Pausata et al., 2012). AO is characterized by winds circulating counterclockwise around the Arctic at around 55°N latitude, (Thompson and Wallace, 2000). In a positive AO phase, surface pressure in the polar region is abnormally low and strong winds around the pole confine cold air masses in the Arctic region; otherwise, more Arctic cold air dives south and increases storminess in the mid-latitude~~s~~ regions

(Thompson and Wallace, 2000). Oswald et al. (2015) hypothesized that observed higher summertime O_3 levels in the northeast US was associated with less storminess in a positive AO phase. Some modeling studies suggested a weak impact from stratosphere-tropospheric exchange of O_3 on the lower troposphere over the Atlantic basin during a positive AO year (Brand et al., 2008; Hess and Lamarque, 2007; Lamarque and Hess, 2004). The impact of AO on surface O_3 in the northeast US needs to be further investigated using long-term surface measurement data.

Our study used long-term observations at seven rural sites in the Northeast US. Five are located in rural New Hampshire (NH) and two are in rural New York (NY) State. Although numerous studies have been conducted to understand the distributions of surface CO and O_3 in the northeast US and their controlling mechanisms (e.g. Bae et al., 2011; Hegarty et al., 20079; Lai et al., 2012; Mao and Talbot, 2004; Schwab et al., 2009; Zhou et al., 2007), little work was done on baseline CO and O_3 using long-term measurement data for the region. Here, the trends of baseline CO and O_3 were examined at each site for the time period of 2001–2010, and regional to global emissions and large scale circulation patterns were investigated for their roles in the interannual and seasonal variation of baseline CO and O_3.

2 Methods and data

2.1 Measurement data

The seven rural sites selected in this study (Table 1 and Fig. 1) are within a few hundred kilometers of each other. Their elevation varies between 18 and 2100 m. Measurements of CO, O_3, wind direction, wind speed, and relative humidity at Appledore Island (AI), Castle Spring (CS), Mount Washington (MWO), Pack Monadnock (PM), and Thompson Farm (TF) were conducted by the University of New Hampshire (UNH) AIRMAP Observing Network (http://www.eos.unh.edu/observatories/data.shtml). The time resolution of the continuous year-

round measurements at these five sites was one minute. At AI, CO was measured seasonally from May to September over 2001–2006 and year round over 2007–2011, and O_3 was measured seasonally from May to September over 2002–2007 and year-round over 2008–2011. All of the measurements have undergone rigorous quality controls and t~~T~~he description of CO and O_3 measurement techniques from the UNH AIRMAP sites can be found in Mao and Talbot (2004). Additionally, hourly data of solar radiation flux were available at TF over January 2002–December 2010 from the Climate Reference Network (CRN) run by the National Ocean and Atmospheric Administration (NOAA) (http://www.ncdc.noaa.gov/crn/~~data access~~). The one-hour measurement data of CO, O_3, wind direction, wind speed, and relative humidity at Whiteface Mountain (WFM) and Pinnacle State Park (PSP) began around 1996 (Table 1). The description of CO and O_3 measurement techniques for WFM and PSP can be found in Brandt et al. (2015) and Schwab et al. (2009). The time in all of the datasets was expressed in coordinated universal time (UTC), i.e. local time +5 h for non-daylight saving time and +4 h for daylight saving time (March–November).

2.2 Quantification of baseline CO and O_3

The local afternoon time window (18:00–24:00 UTC) was selected to avoid including the data representing nighttime depletion of O_3 due to dry deposition and titration (Talbot et al., 2005). The planetary boundary layer (PBL) is well mixed in the afternoon. The monthly 10th percentile mixing ratio of CO at AI, CS, PM, TF, and PSP was used to represent the baseline CO levels. As MWO and WFM are located atop the mountains, they are far less impacted by local anthropogenic emissions. Therefore, monthly median values of CO were selected at MWO and WFM to represent the baseline level. To determine baseline O_3 levels, we first created a subset of O_3 data by using the O_3 mixing ratios corresponding to CO mixing ratios below the monthly 10th

234 percentile values at AI, CS, PM, TF, and PSP and monthly median values at MWO and WFM.
235 The monthly median values of this subset were then defined as the baseline O_3 levels for
236 respective sites.

237 **2.3 Datasets**

238 The NAO index is a measure of the intensity of NAO, which is defined based on the leading
239 empirical orthogonal function of the normalized sea level pressure difference between the
240 subtropical high and the subpolar low using the National Centers for Environmental
241 Prediction/National Center for Atmospheric Research (NCEP/NCAR) reanalysis (Barnston and
242 Livezey, 1987). The AO index was obtained by projecting the daily 1000 hPa geopotential height
243 anomalies poleward of 20°N onto the loading pattern of the AO (Thompson and Wallace, 2000).
244 The Climate Prediction Center of NCEP (http://www.cpc.ncep.noaa.gov/data/teledoc/
245 telecontents.shtml) routinely monitors the primary teleconnection patterns. Monthly climate
246 index values of NAO and AO were used in this study to understand the roles of global transport
247 of atmospheric species via large-scale atmospheric circulation.

248 The Global Fire Emission Data (GFED) combines satellite information of fire activities
249 and vegetation productivities, and contains the gridded monthly burned area and fire emissions.
250 GFED 3 (http://www.globalfiredata.org/) was used in this study to estimate the biomass burning
251 emissions of CO over Russia, Canada, California, and Alaska. Data were available for 2001–
252 2010 at 0.5°× 0.5°horizontal resolution. Monthly mean global CO columns with 1°× 1° resolution
253 obtained from the Measurements of Pollution in the Troposphere (MOPITT) instrument on the
254 satellite Terra (https://www2.acd.ucar.edu/mopitt/) were used for the time period of 2001–2010
255 over grids containing Russia, Canada, Alaska, and California, when wildfire CO emissions in
256 these grids calculated from GFED were larger than 1 g $m^{-2}$$month^{-1}$.

Monthly wind, geopotential height, temperature, relative humidity (http://www.esrl.noaa.gov/psd/data/gridded/data.ncep.reanalysis.html), and potential vorticity (PV) (http://rda.ucar.edu/datasets/ds090.0) with a spatial resolution of 2.5°× 2.5° from the NCEP/NCAR Global Reanalysis Products were used for meteorological conditions and for identifying stratospheric intrusion.

The dataset representing O_3 of stratospheric origin, constructed by Liu et al. (2013) (ftp://es-ee.tor.ec.gc.ca/pub/ftpdt/Stratospheric%20Climatology/), was also used to verify the contribution of stratospheric O_3 to the two mountain sites and the decadal trends there. This dataset included monthly amounts of stratospheric O_3 from the surface to 26 km altitude with 5°× 5°× 1 km spatial resolution from the 1960s to the 2000s.

Mean sea level pressure data were obtained from NCEP-DOE Reanalysis 2 (http://www.esrl.noaa.gov/psd/data/gridded/data.ncep.reanalysis2.html). The dataset is six hourly with a spatial resolution of 2.5°×2.5°. The data were used to identify and quantify the cyclones that passed over the northeast US.

2.4 Mid-latitude cyclone identification and tracking

Many algorithms have been developed since the 1970s to identify mid-latitude cyclones (Hu et al., 2004; Murazaki and Hess, 2006; Racherla and Adams, 2008). The algorithm developed by Bauer and Del Genio (2006) was adopted in this study to track the sea level pressure minima. The first step of the algorithm was to search for the local minimum by a 2 grids × 2 grids matrix. The next step was to search for the local (within 720 km) minimum in the next 6 h time step, assuming that a cyclone cannot move faster than 120 km h^{-1}, the same criterion used by Bauer and Del Genio (2006). If more than one local minimum was found, the point with the lowest sea level pressure was designated as the center of a cyclone.~~the center of a cyclone was obtained.~~ Two more criteria were applied, its duration > 24 h and central pressure ≤ 1020

hPa. Long-term cyclone frequency statistics were calculated for the northeast US (37.5–47.5°N, 67.5–82.5°W).

2.5 Statistical methods

The open-air package in the statistical programming language R 3.0.2 was used to determine whether a rate of change was statistically significant. Trends in baseline CO and O_3 were reported using SenTheil slopes from the non-parametric Mann–Kendall analysis in ppbv yr^{-1} with 90 % confidence intervals. Pearson correlation was computed to determine the relation between variables (e.g. baseline CO, baseline O_3, NAO index, relative humidity). The Student t test was conducted to verify statistical significance ($\alpha = 0.10$).

To quantify the contribution to a location of interest from biomass burning emissions over an area, we applied the following linear regression models (Wotawa et al., 2001):

$$CO = a_0 + a_1 E \quad (1)$$

Where CO is the mixing ratio of baseline CO at each site, E the total CO column over the area, a_0 the intercept value, and a_1 the slope value. The combined effect of biomass burning emissions from Russia (E_{Russia}) and Canada (E_{Canada}) was computed using Eq. (2):

$$CO = b_0 + b_1 E_{Russia} + b_2 E_{Canada} \quad (2)$$

where b_0, b_1, and b_2 are regression parameters. Note that E_{Russia} and E_{Canada} were found to be the two emissions sources that contributed significantly to the baseline CO at the seven sites of our study, which is why only these two sources were included in the regression.

3 Results and discussions

3.1 General characteristics

3.1.1 Baseline CO

Baseline CO at CS, MWO, PM, TF, and PSP had maxima uniformly in March and minima in varying months over August–October (Fig. 2a and b). Averaged annual maxima were 191 ppbv at CS, 180 ppbv at MWO, 155 ppbv at PM, 164 ppbv at TF, and 189 ppbv at PSP over their respective time periods (Table 1). Averaged annual minima were 131 ppbv in August at CS, 142 ppbv in September at MWO, 109 ppbv in October at PM, 113 ppbv in August at TF, and 128 ppbv in October at PSP. At AI, year-round data were available during 2007–2010, a much shorter time period compared to those at other sites. The seasonal cycles at AI were consistent with other sites, with the average annual maximum 149 ppbv in March and minimum 103 ppbv in September. Previous studies suggested that the annual maximum in cold months resulted from residential heating, vehicle cold starts, and less loss from oxidation by OH, while the annual minimum in fall, instead of in June–July when solar radiation and hence OH concentrations reach annual maxima, was probably the combined effect of biomass burning emissions, mobile combustion emissions, and loss from oxidation by OH (Kopacz et al., 2010; Miller et al., 2008).

The annual cycle at WFM was different from those at all other sites, with an annual maximum of 144 ppbv in July and minimum of 103 ppbv in December averaged over January 2001–December 2010 (Fig. 2b). To investigate the potential reasons for this different behavior, the data at WFM were compared with those at MWO, a site with slightly higher elevation (2 km a.s.l.) located 208 km to the east (Fig. 1). WFM and MWO are 128 km southwest and 217 km southeast, respectively, from Montreal, the 9th largest city in North America. Over 2001–2009, averaged summertime baseline CO (141 ppbv) at WFM was comparable to that (145 ppbv) at MWO, while averaged wintertime baseline CO (108 ppbv) at WFM was 60 ppbv or 36 % less than that (168 ppbv) at MWO (Fig. 2a and b). This wintertime contrast was probably associated with the large difference between the frequency distributions of wind direction at the two sites.

There were 4.7 % of the air masses at WFM from the northeast (22.5–67.5°), compared to 75.4 % of the air masses at MWO from the northwest (247.5–337.5°), the general direction of Montreal. This indicates that MWO was frequently exposed to northwesterly winds carrying air masses potentially influenced by anthropogenic emissions in Montreal, while such influences were rare at WFM. Consequently, much lower baseline CO was found at WFM than at MWO.

From April 2001 to December 2010, baseline CO decreased significantly at a rate of −2.5 ppbv yr^{-1} at TF, −4.3 ppbv yr^{-1} at PSP, and −2.8 ppbv yr^{-1} at WFM. Baseline CO decreased at a rate of −2.3 ppbv yr^{-1} at MWO over April 2001–March 2009 and −3.5 ppbv yr^{-1} at PM over July 2004–October 2010 (Table 2). Unlike all other sites, CS exhibited an increasing trend of 2.8 ppbv yr^{-1} over April 2001–June 2008. Prior to May 2003, the mixing ratio of baseline CO at CS was similar to that at TF. After May 2003, baseline CO at CS was ~ 30 ppbv higher than that at TF and PM (Fig. 2a), resulting in the overall increasing trend. The reasons for such unusually high values at CS are unknown.

The U.S. EPA reported a decrease of 52 % in the national average of annual second highest 8 h mixing ratios of CO from 2001 to 2010 (EPA, 2012), corresponding to a rate of −7.8 ppbv yr^{-1} (for an decadal average mixing ratio of ~ 150 ppbv), which was larger than that at any of our sites. Because EPA's trend was estimated using measurements mainly from urban sites with higher concentrations and also focused on the high end of the distribution, it is expected to show larger changes compared to the trend of baseline levels at rural or remote sites from this study, with influence of direct anthropogenic emissions removed.

The total CO column from MOPITT retrievals over the eastern US was found to decrease at a rate of 1.4% yr^{-1} (or −2.1 ppbv yr^{-1} for a decadal average mixing ratio of ~ 150 ppbv) from 2000 to 2011 (Worden et al., 2013), which was comparable to that of the baseline CO in this

study. These significant decreasing trends of baseline CO and total column CO were probably associated in large part with anthropogenic CO emissions reductions worldwide (Gratz et al., 2014). Globally, anthropogenic CO emissions showed a slight decrease of ~ 1% from 1990 to 2010 (Granier et al., 2011). In the US and Europe, total anthropogenic CO emissions declined at a rate of −3 %yr−1 from 2000 to 2010, while increasing trends were found in India (~ 1.5% yr^{-1}) and China(~ 3% yr^{-1}) (Granier et al., 2011). A decreasing trend in CO emissions in China since 2005 was suggested by Tohjima et al. (2014) and Zhang et al. (2009).

3.1.2 Baseline O_3

The baseline O_3 concentrations from all sties ranged from 22 ppbv in the fall to 56 ppbv in spring, consistent with baseline levels in the Eastern US that were quantified using a principal component analysis and backward air parcel trajectories by Chan and Vet (2010). The time series of baseline O_3 at all sites showed averaged annual maxima in April and minima in August–October (Fig. 2c and d). Annual maxima averaged over their respective periods at the seven sites occurred all in April and were very close in magnitude, ranging from 47 to 51 ppbv. In comparison, averaged annual minima at the seven sites displayed distinct difference in magnitude and timing, varying over 28–37 ppbv, occurring in August at CS, September at AI and PM, and October at TF, PSP, MWO, and WFM. Studies have suggested that monthly surface O_3 over remote continental areas generally had a spring maximum, attributed to enhanced stratospheric input and hemispheric wide photochemical production (Monks, 2000; Parrish et al., 2013). Here, the fact that baseline CO had annual maxima in spring suggested that the springtime annual maxima of baseline O_3 were possibly associated with photochemical processing of O_3 precursors including CO and VOCs that had been built up overwinter on a hemispherical scale (Kopacz et al., 2010; Penkett et al., 1993).

A close examination using the Mann–Kendall test suggested no significant trends in baseline O_3 during the study period at all sites (Table 2). Similar results were found in Mace head, Ireland, which is located on the western coast of Europe (Derwent et al., 2007). From 1987 to 1997, baseline O_3 at Mace Head had a significant increasing trend of 0.14 ppbv yr^{-1} followed by a small increase over 1997–1999, and stabilized over 2000–2007 (Derwent et al., 2007).

IPCC (2001) suggested that the change of long-term trends in baseline O_3 could be driven by CH_4 oxidation in the presence of NO_x. In a polluted region, O_3 is produced by photochemical reactions of nonmethane hydrocarbons (NMHCs) and NO_x (West et al., 2006). In the global troposphere, CH_4 is the primary anthropogenic VOC (Fiore et al., 2002) and affects global background mixing ratios of O_3 due to its long lifetime (8–9 years). Derwent et al. (2007) found the change of baseline O_3 in Mace Head followed the mixing ratios of baseline CH_4 over 1992–2007. West et al. (2006) found that reducing global anthropogenic CH_4 emissions by 20% beginning in 2010 would reduce O_3 mixing ratios globally by ~ 1 ppbv in 2030. Globally, the growth rate of CH_4 declined from ~ 13 ppbv yr^{-1} in the early 1980s to near zero over 1999–2006 (WMO, 2012). Since 2007, atmospheric CH_4 was increasing again with an average rate of ~ 3 ppbv yr^{-1} (WMO, 2012). These changes in CH_4 mixing ratios can potentially lead to changes in baseline O_3 mixing ratios.

On the other hand, global NO_x emissions did not change overall during the study period (Granier et al., 2011). Granier et al. (2011) reported that annual NO_x emissions decreased at a rate of 1.5 Tg yr^{-1} in western Europe, 0.7 Tg yr^{-1}in central Europe, ~ 5 Tg yr^{-1} in the US over 2001–2010, while increased at a rate of ~ 5 Tg yr^{-1} in Chinaand ~ 1.5 Tg yr^{-1} in India. Xing et al. (2015) found varying trends in NO_x mixing ratios over 1990–2010, with 4.1% in China, −1.4% in the US, and −1.2% in Europe. The annual rates of change in NO_x concentrations were

394 comparable to those in emissions (Xing et al., 2015). This suggests that increasing CH_4 and
395 opposite trends of NO_x emissions worldwide probably contributed to the insignificant trends in
396 baseline O_3 over the northeast US during 2001–2010.

397 **3.2 Seasonal variation of decadal trends in baseline CO and O_3**

398 Generally a decreasing trend was found in baseline CO and no trend in baseline O_3
399 during the decade 2001–2010 as shown in the previous section. However, trends of baseline CO
400 and O_3 were found to vary by season (Table 2). Baseline CO at CS was anomalously high since
401 May 2003 (Fig. 2a) and had increased over the decade in all seasons. As the reasons for the
402 unusually high values at CS are unknown, baseline CO at CS was not included in the subsequent
403 discussion.

404 In spring and winter, baseline CO at PM, TF, and PSP decreased significantly at a rate
405 between −6.5 to −3.7 ppbv yr^{-1}, while no significant decreasing trends were found at the two
406 highest sites MWO and WFM (Table 2). In summer, baseline CO at MWO, PM, TF, and PSP
407 showed decreasing trends varying between −5.5 and−4.3 ppbv yr^{-1}. In fall, baseline CO at all
408 sites decreased significantly at rates varying between −6.4 and −3.2 ppbv yr^{-1}.

409 The overall insignificant change of baseline CO at MWO and WFM in spring and winter
410 could be due to the combined effect of decreasing US emissions and increasing Asian emissions.
411 MWO and WFM are the highest sites situated close to the top of the daytime convective
412 boundary layer, which are more likely impacted by free tropospheric air compared to other sites.
413 Thus, the impact of continental to intercontinental transport could be just as important there, and
414 perhaps at times more important, than regional transport. CO emissions in the US declined at a
415 rate of ∼ −3 $\%yr^{-1}$ over 2000–2010, while an overall increasing trend was seen in China over
416 1999–2010, despite a small decrease since 2005 (Granier et al., 2011; Tohjima et al., 2014).

Liang et al. (2004), using GEOS-Chem model simulations, found that Asian influence was strongest in spring in the North Pacific lower troposphere, due to the combined effect of efficient ventilation of the Asian boundary layer via midlatitudinal cyclones and convection, long lifetime of CO, and strong springtime biomass burning emissions in southeastern Asia. The same study also found that the Asian influence weakened in summer due to the shorter lifetime of CO and continental export driven most often by convective injection to the upper troposphere, while particularly strong transpacific transport events occurred in spring and winter (Liang et al., 2004).

In fall, baseline O_3 did not show significant trends at any of the sites (Table 2). In summer, baseline O_3 showed distinct decreasing trends of −3.1 ppbv yr^{-1} at AI, −4.7 ppbv yr^{-1} at both MWO and WFM during their respective time periods, and no trends were found at other sites (Table 2). TF was the only site where baseline O_3 increased significantly at a rate of 2.4 ppbv yr^{-1} in spring and 2.7 ppbv yr^{-1} in winter over 2001–2010, while other sites showed no trends during the two seasons.

Tropospheric O_3 has been changing over the past four decades in response to changes in anthropogenic and natural emissions, stratosphere-tropospheric exchange, pollution transport pathways and O_3 photochemistry (Parrish et al., 2013). Therefore, it was hypothesized that the following factors may have contributed to the significant decreasing trends in summertime baseline O_3 at AI, MWO, WFM and significant increasing trends in springtime and wintertime baseline O_3 at TF:

1. Decreasing and increasing stratospheric intrusion in summer and winter – spring, respectively;

2. Decreasing and increasing continental to intercontinental transport of anthropogenic and natural O_3 precursors in summer and winter – spring, respectively;

3. Decreasing emissions of NO_x from electric power generation and motor vehicles; and

4. Changing pollution transport pathways in winter, spring, and summer.

Factor #1 was examined using PV data, as one of the physical characteristics of stratospheric air is high value of PV. Time series of PV at 350 K showed no trend in PV over the northeast US during the decade (Fig. 3a). There appeared to be distinct annual cycles in PV with maxima in winter and minima in summer, averaged 1.81×10^{-8} and 1.05×10^{-8} $m^2s^{-1}kg$, respectively (Fig. 3a). Hence, stratospheric intrusion probably had a larger impact on the surface in winter-spring than in summer, which was supported by previous studies (James et al., 2003; Stohl et al., 2003). Such impact would more likely reach higher than lower elevation locations. No trends in baseline O_3 at the two highest sites MWO and WFM appeared to be consistent with what the time series of PV suggested. Moreover, TF, near the sea level (18 m a.s.l.), was less likely influenced by stratospheric intrusion than all other sites. These points were verified using the stratospheric O_3 during 2001–2010 from Liu et al. (2013), which suggested, on seasonal average in the area including all our sites, no contribution to the lowest layer (0.5 km) in summer, or no significant trends in such contribution in winter-spring. Therefore, it seemed unlikely that stratospheric intrusion contributed to the springtime and wintertime increasing trends in baseline O_3 at TF.

Significant increases have been reported by Cooper et al. (2012) in springtime and wintertime free tropospheric O_3 over North America, particularly in air masses originating from East Asia. The western US with elevated terrain was much more likely to be influenced by descending free tropospheric air than the eastern US (Cooper et al., 2012). Even if air masses rich in O_3 originating from East Asia reached the US East Coast, they would most likely have a

stronger impact on elevated sites. The fact of no trends at any of the elevated sites in spring or winter suggested that long-range transport of O_3 and its precursors from Asia was probably not a cause of increasing springtime and wintertime baseline O_3 at TF (Factor #2).

In summer, continental export from East Asia is weaker (Wild and Akimoto, 2001) and Asian emissions have less impact on US surface O_3 relative to domestic emissions than in winter and spring (Reidmiller et al., 2009), which ruled out the effect of long-range transport of Asian emissions on summertime trends in baseline O_3 at our sites. Summer sees the peak of forest fires (Wotawa et al., 2001). Therefore, changes in emissions of CO and other O_3 precursors from biomass burning could influence the trends in summertime baseline O_3 and CO (Sect. 3.3.1).

Further analysis suggested that decreasing urban emissions of NO_x quite likely contributed to the rise in springtime and wintertime baseline O_3 at TF (Factor #3). Tropospheric NO_2 column over the US declined by 41% in spring and 33% in summer during the period of 1996–2011 (Cooper et al., 2012). Emissions of NO_x in the US were reduced by 48% over 1990–2010, largely due to control of emissions from power plants and mobile sources (Xing et al., 2013). The Northeast US Urban Corridor, extending from Washington D.C. in the south to Boston in the north, was dominated by mobile combustion emissions of NO_x. Annual mixing ratios of NO_2 in New York City decreased at a rate of -0.3 ppbv yr^{-1}over 1980–2007 (Buckley and Mitchell, 2011). In winter and early spring with weakened photochemical production, decreased NO_x emissions in urban areas could cause less loss of O_3 via titration by NO (Liu et al., 1987; Jacob et al., 1995; Frost et al., 2006; Jonson et al., 2006), and the result could be enhanced O_3 mixing ratios in urban plumes (Cooper et al., 2010; Wilson et al., 2012). From measurements at our sites, data points of O_3 were selected corresponding to wind from the urban corridor. It was found that the 10th percentile mixing ratio of O_3 at TF in air masses from the urban corridor

had been increasing at a rate of 1.81 ppbv yr^{-1} ($p = 0.05$) in spring and 1.52 ppbv yr^{-1}($p < 0.01$) in winter (Fig. 3b and c). This strongly suggests that decreased NO_x emissions in the urban corridor likely had a significant impact on springtime and wintertime baseline O_3 at TF whereas had no similar effects at other sites. In summer with strong photochemistry, decreased emissions of O_3 precursors could lead to reductions in peak summertime O_3 concentrations at surface continental sites (Cooper et al., 2012; Parrish et al., 2013). No significant change was found in summertime 10th percentile mixing ratios of O_3 in air masses from the urban corridor at TF, which was consistent with the relatively constant summertime baseline O_3 at TF as aforementioned.

The implementation of the Acid Rain Program and the NO_x Budget Trading Program (NBP) also reduced NO_x emissions from the power plants (Xing et al., 2013). In the Ohio River Valley, where power plants dominate, both NO_2 column and NO_x emissions decreased by 38 and 34% over 1999–2005 (Kim et al., 2006). However, the 10th percentile mixing ratio of O_3 in air masses from the southwest did not show any significant change in winter, spring, and summer at PSP, which is located to the northeast of the Ohio River Valley (Fig. 3b–d).

There is interannual variability in transport pathways, temperature, water vapor, solar radiation, and natural emissions (e.g., lightning, forest fires, and vegetation). A close examination of the NOAA CRN data revealed that springtime solar radiation at TF was increasing at a rate of 24.5 W m^{-2} yr^{-1} ($p = 0.03$) over 2002–2010, with the lowest value of 432 Wm^{-2} in 2002 (Fig. 3a), while no significant trend was found in winter. Without the value in spring 2002, the solar radiation flux at TF increased at a rate of 9.4 W m^{-2} yr^{-1}in spring (p = 0.02). This trend in springtime solar radiation at TF was possibly related to cloudiness in response to changing cyclone activity associated with varying atmospheric circulation, which

could have affected baseline O_3. More frequent cyclone activities, wetter conditions associated with the North Atlantic storm track parallel to the eastern US coast could be possible factors leading to the very low solar radiation flux in spring 2002. Further research is warranted to fully understand what may have caused this phenomenon. The impact of changes in weather conditions and large scale circulation on baseline O_3 was further explored in the following section.

3.3 Factors controlling baseline CO and O_3 in spring and summer

This section further identifies factors impacting the variation of baseline CO and O_3. Emphasis was placed on spring and summer, when there are strong intercontinental transport and photochemistry involving O_3 and CO (Cooper et al., 2010; Emmons et al., 2003), as well as exceedances of NAAQS.

3.3.1 Impact of wildfires in summer

Large interannual variability in global CO mixing ratios was attributed to variations in biomass burning emissions (Novelli et al., 2003; Wotawa et al., 2001). Studies (Hecobian et al., 2011; Oltmans et al., 2010) suggested that biomass burning effluents from Russia and Canada flowed into North America. In addition, California and Alaska were two US states with considerable fire emissions of CO, which reportedly impacted the air quality over North America (McKendry et al., 2011; Real et al., 2007).

Fire emissions of CO in summer were estimated using the GFED dataset and MOPITT retrievals (Fig. 4a and b). The GFED data suggested that massive wildfires occurred in Russia in 2002, 2003, and 2008 with annual CO emissions of 42.1, 71.1, and 35.8 Tg, respectively. Annual fire emissions from Canada were 17.4 Tg in 2004 and 18.3 Tg in 2010. In Alaska, the largest fires occurred in 2004 with 13.1 Tg CO emitted, while in California the largest fire emissions of

CO were 1.3 Tg in 2008. From 2001 to 2010, the total CO emissions from wildfires in Russia, Canada, Alaska and California varied from 19.9 to 84.3 Tg, with the lowest and the highest in 2007 and 2003, respectively.

To quantify contributions of wildfires from these four areas to summertime baseline CO levels at our sites, a linear regression model was used together with MOPITT total CO column retrievals. Monthly CO columns were first correlated with monthly GFED fire emissions of CO for the four areas. The correlation coefficients were 0.89, 0.81, 0.81, and 0.84 ($p < 0.01$ for the four values) for Russia, Canada, California, and Alaska, respectively, suggesting that the variability in total column CO over those areas was dominated by that of fire emissions.

Further, it was found that the contributions of fire emissions from Russia and Canada to the variability of summertime baseline CO at the 5~~6~~ sites were averaged to be 3~~7~~8 and 22%, respectively (Table 3), and their combined contribution was averaged to be 41%.Contributions from Alaska and California were negligible at these six sites. Globally, there is approximately 1 billion ha closed forest in the boreal region, about two thirds of which is situated in Russia (Harden et al., 2000). CO emissions from wildfires in Russia and Canada contributed 49.5 and 29.6%, respectively, to the total CO emissions from wildfires in Northern Hemispheric midlatitudes (30–90°N). Understandably, baseline CO was well correlated to wildfires in Russia and Canada at most sites except at PSP.

The insignificant correlation between baseline CO at PSP and wildfires emissions from Russia and Canada was possibly due to less dynamical circulation at the site. PSP had the lowest wind speed of 0.47 m s^{-1} amongst all sites based on surface wind speed averaged over summers of 2001–2010 (Fig. 5a). This appeared to be consistent with the position of PSP relative to the pressure systems throughout the year (Fig. 5b–e). The climatological seasonal maps of sea level

555 pressure suggest that PSP is located either on the periphery of the subtropical high in summer –
556 fall, or the periphery of the North American trough, where wind tends to be the weakest. In
557 comparison, other sites are either located at the top of the boundary layer, and/or tend to be
558 positioned within the North American trough, more directly under the influence of the westerly
559 wind often facilitating global transport.

560 Since wildfires provide a substantial source of NO_x and hydrocarbons, O_3 is expected to
561 form in fire plumes. Some of these air pollutants live long enough to travel over long distances,
562 which could elevate baseline O_3 globally (Jaffe et al., 2004). Corresponding to the largest fire
563 emissions in summer 2003 in Russia (Fig. 4a), baseline CO in that season at all sites reached the
564 decadal maxima, and baseline O_3 was the highest of all summers at AI, CS, MWO, TF, and
565 WFM (Fig. 4c and d). Jaffe et al. (2004) also suggested that emissions from Siberia forest fires in
566 summer 2003 were transported to North America resulting in enhancements of 23–37 and 5–9
567 ppbv in summertime baseline CO and O_3, respectively, at 10 sites in Alaska, Canada, and the
568 Pacific Northwest.

569 The second largest summertime baseline CO mixing ratio of the decade was found in
570 summer 2004 at ~~CS,~~ TF, and WFM (Fig. 4c), although the total CO emissions from wildfires in
571 Russia and Canada during that season was 20.4 Tg, 16% smaller than 24.4 Tg, the decadal
572 (2001–2010) average annual CO emissions from the two countries. Over Alaska, the
573 geopotential height in summer 2004 was ~ 40 gpm higher than normal years (Fig. 6a–c). This
574 relatively higher pressure field led to drier and warmer conditions over Alaska and southwestern
575 Canada with 82% relative humidity and 12°C surface temperature, the driest and warmest of the
576 decade (Fig. 6d). Such weather conditions are conducive to occurrence of wildfires. In summer
577 2004, CO emissions from wildfires in Canada and Alaska contributed 48.5 and 36.5%,

578 respectively, to the Northern Hemispheric total, compared to the decadal (2001–2010) average
579 contributions of 49.5, 10.6, and 29.6% from Russia, Alaska, and Canada, respectively.
580 Correspondingly, the 13.1 Tg CO emissions from wildfires in Alaska were the largest over the
581 decade, and the 17.4 Tg CO emissions from wildfires in Canada were the second largest of the
582 decade, following the largest in summer 2010 (Fig. 4a). On the other hand, the streamlines over
583 Canada suggested an unusually strong northeasterly component in summer 2004. The high
584 pressure system over Alaska and southwestern Canada most likely strengthened the westward
585 transport of wildfires effluents from Alaska and Canada (Fig. 6c). The combination of these two
586 factors resulted in efficient transport of massive CO emissions from fires over Alaska and
587 Canada. Smoke from these fires over the continental United States was observed in satellite
588 images of aerosol optical depth (AOD) from the GOES (Geostationary Operational
589 Environmental Satellites) (Kondragunta et al., 2008) and MODIS (Moderate Resolution Imaging
590 Spectro-radiometer) aboard Terra (Mathur, 2008), and extensive plumes of enhanced CO
591 concentrations were captured in MOPITT (Measurements of Pollutants in the Troposphere)
592 retrievals (Pfister et al., 2005).

593 Mann–Kendall trend analysis indicated no significant decreasing trends in biomass
594 burning emissions from Alaska, Canada, and California. In contrast, CO emissions from
595 wildfires in Russia decreased at a rate of −0.51 Tg yr^{-1} (p = 0.10). Summertime baseline CO at
596 MWO, PM, TF, and PSP decreased at a rate between −5.5 and −4.3 ppbv yr^{-1} and baseline O_3 at
597 AI, MWO, and WFM decreased at a rate between −4.7 and −3.1 ppbv yr^{-1} (Sect. 3.2). Based on
598 regression analysis, as a result of a 0.51 Tg yr^{-1} decrease in CO emissions from wildfires in
599 Russia, baseline O3decreased by 0.04–0.07 ppbv yr^{-1} (p = 0.08–0.10) at AI, MWO, WFM, and
600 CS, while baseline CO declined by 0.14–0.22 ppbv yr^{-1} (p = 0.01–0.10) at AI, TF, MWO, and

WFM. Hence, the decreasing trend of biomass burning emissions in Russia was likely a major factor causing the decreasing trends in baseline CO and O_3 in summer at our sites.

3.3.2 Impact of cyclone activity and AO in summer

Meteorology is another factor that can influence summertime baseline CO and O_3 across the northeast US over 2001–2010–. Oof all the meteorological variables, midlatitude cyclone frequency is an important one that can impact regional air quality greatly. It affects not only boundary layer ventilation, humidity, solar radiation, and temperature but also general circulation of the regional atmosphere (Leibensperger et al., 2008).

Time series of summertime counts of cyclones in the northeast US showed strong interannual variability (Fig. 7a). The counts of cyclones in 2003, 2006, 2008, 2009, and 2010 were greater than 12, the average of summer 2001–2010. Summer 2009 experienced the largest number of cyclones (20) passing the northeast US during the 2001–2010 period. Other summers experienced below-average cyclones. No overall trend was found in the counts of cyclones during the study period. Our calculated numbers of cyclones were consistent with the results for the same years from Leibensperger et al. (2008) and Bauer and Del Genio (2006).

In summer, cyclones tend to move around the 500 hPa vortex, which is over the cold Arctic Ocean with broadly symmetric flow around it (Serreze et al., 2007). On the North American side, the high latitude flow on the 500 hPa pressure level has a southward component, which tends to steer systems away from the Arctic Ocean (Fig. 7b). Composite analyses associated with years of strong (2003, 2006, 2008, 2009, and 2010) vs. weak (2001, 2002, 2004, 2005, and 2007) cyclone activities revealed distinct differences in regional to large scale circulation (Fig. 7c). There turned out to be a pronounced positive difference of ~ 35 gpm centered over Baffin Island (north of the northeast US) and a negative difference of ~ 25 gpm

centered over the northeast US (Fig. 7c). This difference was related to the negative phase of AO (Fig. 7a), when surface pressure is abnormally high in the polar region and low in the midlatitudes (Archambault et al., 2008). In a negative AO season, Arctic lows and westerlies are weaker, leading to more frequent cold-air outbreaks down to Eurasia and the US, and stormy weather over the Mediterranean (Hess and Lamarque, 2007), and ultimately low baseline CO and O_3 across the northeast US.

A case in point was summer 2009 with the largest cyclone count (20) and the strongest negative AO phase (−0.92) of the decade (Fig. 7a). Consistent with earlier results, the difference of 500 hPa geopotential height between summer 2009 and the 10 year average had negative anomalies up to ~ −60 gpm over the North American continent and positive anomalies up to ~ 65 gpm centered near the pole (Fig. 7d). The sea level pressure field (Fig. 7e) featured a pronounced mean low over southern Canada and the streamlines suggested an unusually strong northeasterly component. Indeed, the frequency distribution of wind direction at each site suggested more frequent occurrence of northeasterly wind (22.5–112.5°), with 21% at PM, 9% at MWO, 42% at TF, 11% at PSP, and 13% at WFM (Fig. 8). In summer 2009, the northeast US was more often under the influence of cold frontal passages associated with the largest number of cyclones passing through the region. As a result, the northeast US was exposed most frequently to air masses of Arctic origin. Moreover, emissions from large scale wildfires clearly had global effects as discussed in Sect. 3.3.1. In summer 2009, ~ 11.9 Tg CO, the lowest of the decade, was emitted from wildfires in Russia and Canada (Fig. 7f). Hence, the lowest fire emissions of CO and the most frequent cyclone activities were likely two important factors leading to the lowest summertime baseline CO and O_3 in 2009 at the study sites.

A contrasting case was summer 2003, when AO was negative and 15 cyclones passed the region (Fig. 7a), 25% greater than the decadal mean (12), and yet baseline CO and O_3 at the sites reached the decadal maxima (Figs. 4c, d and 7f). According to the analysis above, baseline CO and baseline O_3 were expected to be lower during this summer than the decadal average as a result of above-average passages of cyclones. However, in summer 2003 CO emissions from Russian and Canadian wildfires were the largest of the decade (Sect. 3.3.1), counteracting the effect of the AO. Another interesting example was summer 2007 which had the lowest cyclone activity of the decade (Fig. 7a), and the total CO emissions from wildfires in Russia and Canada were 13.6 Tg, the second lowest of the decade following summer 2009 (Fig. 7f). The site-average baseline CO and O_3 levels in summer 2007 were below the decadal means. Therefore, the effect of biomass burning may dominate over that of AO and cyclone activity during some summers, while the two worked in concert during others.

Overall, no distinct correlation between counts of cyclones and baseline O_3 was found at most sites (AI, CS, MWO, PM, TF, WFM), while no significant correlation between counts of cyclones and baseline CO was found at any of the sites. The only exception was PSP where the count of cyclones was found to be reasonably anti-correlated with baseline O_3 ($r = -0.56$, $p = 0.05$) in the summer. As discussed in Sect. 3.3.1, PSP was the only site that did not seem to be affected by the Russian and Canadian wildfire emissions as all other sites were, possibly due to its being situated in a region less impacted by large-scale dynamics. Perhaps this very dynamic characteristic cast the site under a predominant influence of synoptic systems, e.g., the Bermuda High and cold frontal passages. As commonly known, high mixing ratios of O_3 in the northeast occur under summertime stagnant, clear sky conditions associated with the Bermuda High (Logan, 1989; Vukovich, 1995; Hegarty et al., 2007; Lai et al., 2012), while low O_3 was often

669 linked to cold fronts which sweep out polluted air leaving much cooler and cleaner air in the
670 northeast (Cooper et al., 2001; Leibensperger et al., 2008; Li et al., 2005). Conceivably, with
671 more frequent cyclones passing the northeast US, lower concentrations of baseline CO and O_3
672 would be expected, and the predominant effect of such synoptic systems could quite likely lead
673 to anticorrelation between the baseline CO/O_3 levels and cyclone activities.

674 **3.3.3 Impact of NAO in spring (March and April)**

675 Wildfires in March and April were scarce, with mean CO emissions of 1.78 Tg in Russia
676 and 0.004 Tg in Canada over 2001–2010, negligible compared to emissions during the fire
677 season (May–September). To focus on the impact of large circulation patterns on baseline CO
678 and O_3 in spring, the May data were excluded to avoid the effect of biomass burning. Springtime
679 baseline O_3 at each site showed strong and consistent interannual variation up to 10 ppbv (Fig.
680 9a). The baseline O_3 mixing ratio averaged at all the seven sites over the decade was 46.5 ppbv,
681 and exceeded the average (>46.5 ppbv) in 2001, 2003, 2005, 2008, 2010, and was below average
682 (≤ 46.5 ppbv) in 2002, 2004, 2006, 2007, 2009 (Fig. 9a).

683 The difference of 850 hPa geopotential height between the lower and higher O_3 years is
684 shown in Fig. 10. There was a pronounced difference up to 40 gpm in the Bermuda/Azores high
685 and ~ −40 gpm in the Icelandic low, which resulted in stronger gradient flow between the two
686 pressure systems and was indicative of the positive phase of NAO~~, known as the positive phase~~
687 ~~of NAO~~. Over 2001–2010, NAO index was significantly positive in 2002, 2004, 2007, 2009 and
688 negative in 2001, 2005, 2008, 2010, which corresponded mostly to the years of below and above
689 the decadal average baseline O_3,respectively. Significant negative correlation was found between
690 the NAO index and baseline O_3 at each site (Table 4)~~(CS: r = −0.75, p = 0.03; MWO: r = −0.68,~~
691 ~~p = 0.03; PM: r = −0.81, p = 0.03; TF: r = −0.81, p < 0.01; PSP: r = −0.58, p = 0.06; WFM: r =~~

692 ~~=0.51, p = 0.10)~~. The negative correlation between baseline O_3 and the NAO index could be a
693 result of multiple factors, such as solar flux, stratosphere-tropospheric exchange, and continental
694 export of O_3 produced in North America. ~~It should be noted that, no significant correlation was~~
695 ~~found between the NAO index and baseline CO at any of the sites, which suggests that NAO is~~
696 ~~not linked to or played an insignificant role in the interannual variability of baseline CO.~~

697 The first possible explanation for the baseline O_3 and NAO index anticorrelation was
698 changes in surface solar radiation flux during positive/negative NAO years. During a positive
699 NAO year, the mean North Atlantic storm track parallels the eastern North American coastline
700 before extending northeastward to near Iceland (Rogers, 1997). This storm track and its
701 associated moisture transport and convergence lead to relatively wet conditions near the eastern
702 US coast (Archambault et al., 2008; Hurrell, 1995). During a negative NAO year, the mean
703 North Atlantic storm track is more zonal (Rogers, 1997), leading to relatively dry conditions near
704 the eastern US coast (Archambault et al., 2008; Hurrell, 1995). At ~~our costal~~ sites around the
705 northeast US coast (CS and TF), significant correlation was found between relative humidity and
706 the NAO index ~~(CS: r = 0.85, p = 0.02; TF: r = 0.64, p = 0.06)~~, while the correlation was weaker
707 at inland, elevated sites (PSP and WFM) ~~(PSP: r = 0.23, p = 0.26; WFM: r = 0.40, p = 0.13)~~
708 (Table 4 and Fig. 9b).

709 During positive NAO years, wetter conditions indicate higher relative humidity and more
710 cloudiness, most likely leading to reduced solar radiation flux near the surface and subsequently
711 less O_3 production. As expected, a significant negative correlation was found between relative
712 humidity and solar radiation ~~(r = =0.67, p = 0.05) (Fig. 9b)~~ and a significant positive correlation
713 between baseline O_3 and solar radiation flux ~~(r = 0.75, p = 0.03)~~ at TF in March and April (Table
714 4 and Fig. 9b). No significant correlation between these variables was found in other seasons.

Another possible explanation for the negative correlation between NAO index and baseline O_3 was the influence of stratospheric intrusion. Dynamically, the North American trough induces descending air on its tailing side and in the upper troposphere it can cause tropopause folding with stratospheric air mixing downward into the troposphere. The difference of the PV patterns between positive NAO years and negative NAO years is illustrated in Fig. 11. Negative anomalies of $\sim -0.6 \times 10^{-9}$ $m^2s^{-1}kg$ were found over the northeast US, suggesting that positive NAO was related to less stratospheric intrusion (Hess and Lamarque, 2007) over the northeast US. This is consistent with lower baseline O_3 levels during positive NAO springs. This was further verified using the stratospheric O_3 dataset constructed by Liu et al. (2013). Stratospheric O_3 was hardly detected at the lowest two layers (i.e., 0.5 and 1.5 km) in April. In March, ~ 40–60 ppbv of stratospheric O_3 reached the lowest layer in our study area in 2004 and 2006–2008 and reached the 1.5 km layer in 2001–2008. The stratospheric contribution to the 0.5 km layer was the largest in March 2008, when NAO was negative (Fig. 9).

The third possible factor affecting baseline O_3 over the northeast US was the effect of North American continental export. During a positive NAO phase, the anticyclonic circulation off the US east coast and the cyclonic circulation across the North Atlantic were amplified with a northward shift (Rogers, 1997). As a result, stronger surface wind was found near 50°N across the North Atlantic basin and into Northern Europe (Hess and Lamarque, 2007). Annual wind speed from the west (247.5–337.5°) was calculated at the study sites (Fig. 9c). Positive correlation was found between surface wind and NAO index at MWO, CS, and TF (Table 4) ~~most sites (MWO: r = 0.76, p = 0.02; CS: r = 0.68, p = 0.06; TF: r = 0.57, p = 0.09)~~. Eckhardt et al. (2004) found that the warm conveyor belt over the northeast US coast occurred ~ 12% more frequently in positive NAO years than in negative NAO years. The ending trajectories of the

warm conveyor belt in positive NAO years extended further eastward into western and northern Europe (Eckhardt et al., 2004). It was suggested that in a positive NAO year, the O_3 produced over the northeast US was less likely accumulated in the region, and was more likely transported faster off the continent and across the Atlantic Ocean. These changes were consistent with the positive anomalies of O_3 observed over northwestern Europe (Christoudias et al., 2012; Eckhardt et al., 2003). Negative correlation, although insignificant, was also found between baseline CO and the NAO index at most of our study sites (Table 4). North American continental export could also impact the variation of baseline CO, while this impact could be confounded by other factors, e.g. stratospheric intrusion. Specifically, during positive NAO years, more continental outflows lead to a decrease in baseline CO, while less stratospheric intrusion wound lead to less dilution of surface CO and thus increase baseline CO levels. Further research is warranted to fully understand the relationship between baseline CO and NAO.

4 Summary

Baseline CO and O_3 at seven rural sites in the northeast US were examined for their seasonal and interannual variabilities during the time period of 2001–2010, and potential mechanisms controlling the variabilities were investigated. It was found that baseline CO at most sites (MWO, PM, TF, PSP, and WFM) decreased significantly at a rate between −4.3 to −2.3 ppbv yr^{-1}, while baseline O_3 was relatively constant. No trends were found in baseline O_3 at all sites probably resulting from relatively constant mixing ratios of CH_4 in the 2000s and opposite rates of change in NOx emissions around the world.

In spring and winter, baseline CO at MWO and WFM did not exhibit a significant trend, possibly a result of the combined effect of decreasing emissions in the northeast US and increasing emissions in Asia. TF, a coastal rural site, was the only location where baseline O_3

761 was found to increase significantly at a rate of 2.4 and 2.7 ppbv yr^{-1} in spring and winter,
762 respectively, most likely caused by the decrease in NO_x emissions over the urban corridor.

763 It was found that interannual variations of baseline CO and O_3 were predominantly
764 influenced by biomass burning emissions, cyclone activities, and NAO. In summer, ~ 38% of
765 baseline CO variability was attributed to CO emissions from forest fires in Russia and ~ 22% to
766 emissions from forest fires in Canada. The lowest mixing ratios of baseline CO and O_3 at most
767 sites in summer 2009 were linked to frequent cyclone activity, which were induced by the
768 unusually weak low pressure system in the Arctic region. In spring, a significant negative
769 correlation was found between baseline O_3 and the NAO index, potentially due to variations of
770 solar flux, stratospheric intrusion, and continental export.

771 On 1 October 2015 the U.S. EPA lowered the NAAQS for ground-level O_3 to 70 ppbv ~~In~~
772 ~~December 2014, the U.S. EPA proposed to tighten the 2008 NAAQS for daily maximum 8-h~~
773 ~~average O_3 from 75 ppbv to a level within a range of 65-70 ppbv~~ ~~to provide~~ to improve
774 protection of public health and welfare ~~(EPA, 2014)~~ (http://www3.epa.gov/ozonepollution/pdfs/
775 20151001overviewfs.pdf). As the O_3 NAAQS are set closer to background levels, states will face
776 ever increasing challenges with regard to fulfilling their obligation for NAAQS attainment.
777 Through this study it was reinforced that, in addition to domestic emission control,
778 intercontinental transport of anthropogenic emissions and wildfires emissions together with
779 meteorological conditions should be considered for an encompassing, cost-effective emission
780 control strategy that accounts for impacts of regional to global emissions and moreover
781 emissions of multi-pollutants (e.g., CO, CH_4, NO_x, and NMHCs). In addition, the relationships
782 between baseline O_3/CO and various factors (e.g. NO_x emission controls, biomass burning
783 emissions, NAO, and AO) examined in this study can also be used as reference point for

784 evaluating global/regional air quality modeling systems that are used in air quality management
785 applications. One limitation of this study is that it was based on ten-year observations, and hence
786 it was unlikely to predict the potential changes in natural emissions and AO/NAO signals as well
787 as their impacts on baseline O_3. Future research is warranted to further address the issues
788 identified in this work on climatological time scales.

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Table 1. Ground stations with geographical coordinates and measurement periods.

Site	Latitude	Longitude	Elevation	Measurement Period (CO)	Measurement Period (O_3)
Appledore Island (AI)	42.97°N	70.62°W	18 m	Jul, 2001- Jul, 2011	Jul, 2002- Mar, 2012
Thompson Farm (TF)	43.11°N	70.95°W	23m	Apr, 2001- Jul, 2011	Apr, 2001- Aug, 2010
Mt. Washington (MWO)	44.27°N	71.30°W	1917m	Apr, 2001- Apr, 2009	Apr, 2001- May, 2010
Castle Spring (CS)	43.75°N	71.35°W	396m	Apr, 2001- Jun, 2008	Apr, 2001- May, 2008
Pack Monadnock (PM)	42.86°N	71.88°W	698m	Jun, 2004- Jul, 2011	Jul, 2004- Oct, 2008
Whiteface Mountain (WFM)	44.40°N	73.90°W	1484 m	Jan, 1996- Dec, 2010	Jan, 1996- Dec, 2010
Pinnacle State Park (PSP)	42.09°N	77.21°W	504 m	Jan, 1997- Dec, 2010	Jan, 1997- Dec, 2010

Note: CO and O_3 at AI were measured seasonally from May to September before 2007/2008. Year-round measurements of CO and O_3 began in May, 2007 and February, 2008, respectively.

Table 2. Trends (ppbv yr^{-1}) of baseline CO and O_3 in spring, summer, fall, and winter. *p*-values are in the parentheses. Boldfaced numbers indicate *p*-value < 0.10.

		Spring		Summer		Fall		Winter		Annual	
Site	Period	CO	O_3	CO	O_3	CO	O_3	CO	O_3	CO	O_3
AI	2002-2010			0.8(0.66)	**-3.1(0.07)**						
CS	2001-2008	3.4(0.06)	0.9(0.65)	2.4(0.19)	-2.9(0.14)	1.1(0.57)	1.5(0.45)	6.1(<0.01)	0.4(0.86)	**2.8(<0.01)**	0.8(0.39)
MWO	2001-2009	-13.2(0.51)	-0.7(0.71)	**-4.5(0.01)**	**-4.7(0.01)**	**-4.4(0.01)**	-0.9(0.64)	-1.7(0.36)	0.1(0.98)	**2.3(<0.01)**	0.7(0.42)
PM	2005-2010	**-6.5(<0.01)**	-1.9(0.39)	**-5.5(<0.01)**	-3.5(0.14)	**-4.2(0.05)**	-3.4(0.11)	**-5.5(0.01)**	0.1(1.00)	**3.5(<0.01)**	0.8(0.43)
TF	2001-2010	**-3.7(0.02)**	**2.4(0.10)**	**-4.5(<0.01)**	-0.1(0.94)	**-3.2(0.04)**	0.2(0.90)	**-4.8(<0.01)**	**2.7(0.09)**	**2.5(<0.01)**	0.8(0.29)
PSP	2001-2010	**-4.5(<0.01)**	1.3(0.43)	**-4.3(<0.01)**	-0.8(0.57)	**-4.2(0.01)**	-1.9(0.23)	**-3.9(0.02)**	-0.7(0.68)	**4.3(<0.01)**	0.7(0.40)
WFM	2001-2010	-0.5(0.78)	0.4(0.83)	-1.9(0.23)	**-4.7(<0.01)**	**-6.4(<0.01)**	0.5(0.76)	-2.1(0.21)	-1.3(0.45)	**2.8(<0.01)**	0.9(0.27)

Table 3. The contributions, in r^2~~R^2~~, of CO emissions from wildfires over Russia, Canada, Alaska, and California to variation (r^2) in baseline CO at each site. The combined effect of wildfire emissions over Russia and Canada was also computed. Boldfaced numbers indicate *p*-value < 0.10.

	Russia		Canada		Alaska		California		Combined	
	r^2~~R^2~~	*p*	r^2~~R^2~~	*p*	r^2~~R^2~~	*p*	r^2~~R^2~~	*p*	r^2~~R^2~~	*p*
AI	**0.39**	**0.01**	0.12	0.15	0.13	0.19	0.12	0.21	**0.41**	**0.02**
CS	~~**0.41**~~	~~**0.01**~~	~~**0.17**~~	~~**0.09**~~	~~0.06~~	~~0.38~~	~~<0.01~~	~~0.92~~	~~**0.41**~~	~~**0.02**~~
MWO	**0.41**	**0.01**	0.13	0.15	0.01	0.77	<0.01	0.88	**0.43**	**0.02**
TF	**0.64**	**0.01**	**0.40**	**0.05**	0.01	0.80	0.03	0.52	**0.65**	**0.01**
PSP	0.11	0.18	0.15	0.11	0.09	0.27	<0.01	0.93	0.16	0.27
WFM	**0.32**	**0.01**	**0.32**	**0.01**	<0.01	0.90	0.01	0.69	**0.38**	**0.03**
Mean	0.37~~0.38~~		0.22		<0.05		<0.03		0.41	

Note: PM was not included due to insufficient data; CS was not included, ~~,~~as mixing ratios of baseline CO at this site were unusually high over May 2003 – June 2008.

Table 4. Correlation coefficient (r) and p-value between the pairs of variables in March and April over 2001 – 2010.

Pair of Variables	CS	MWO	PM	TF	PSP	WFM
NAO index vs Baseline O_3	**-0.75 (0.03)**	**-0.68 (0.03)**	**-0.81 (0.03)**	**-0.81 (<0.01)**	**-0.58 (0.06)**	**-0.51 (0.10)**
NAO index vs Baseline CO	-	-0.51 (0.12)	-0.06 (0.46)	0.30 (0.22)	-0.14 (0.36)	-0.16 (0.34)
Relative humidity vs NAO index	**0.85 (0.02)**	-	-	**0.64 (0.06)**	0.23 (0.26)	0.40 (0.13)
Relative humidity vs Solar radiation flux	-	-	-	**-0.67 (0.05)**	-	-
Baseline O_3 vs Solar radiation flux	-	-	-	**0.75 (0.03)**	-	-
Surface wind speed vs NAO index	**0.68 (0.06)**	**0.76 (0.02)**	-	**0.57 (0.09)**	0.44 (0.12)	-

Note: CO at CS was not included, .as mixing ratios of baseline CO at this site were unusually high over May 2003 – June 2008.

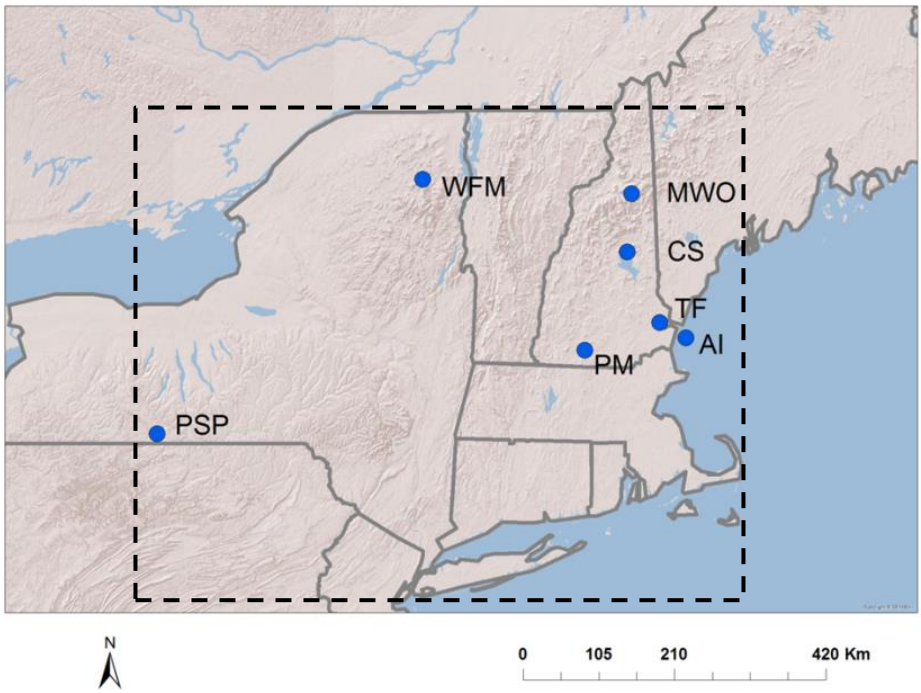

Fig. 1. Map of the Northeast U.S. The seven measurement sites used in the study are marked with blue dots.

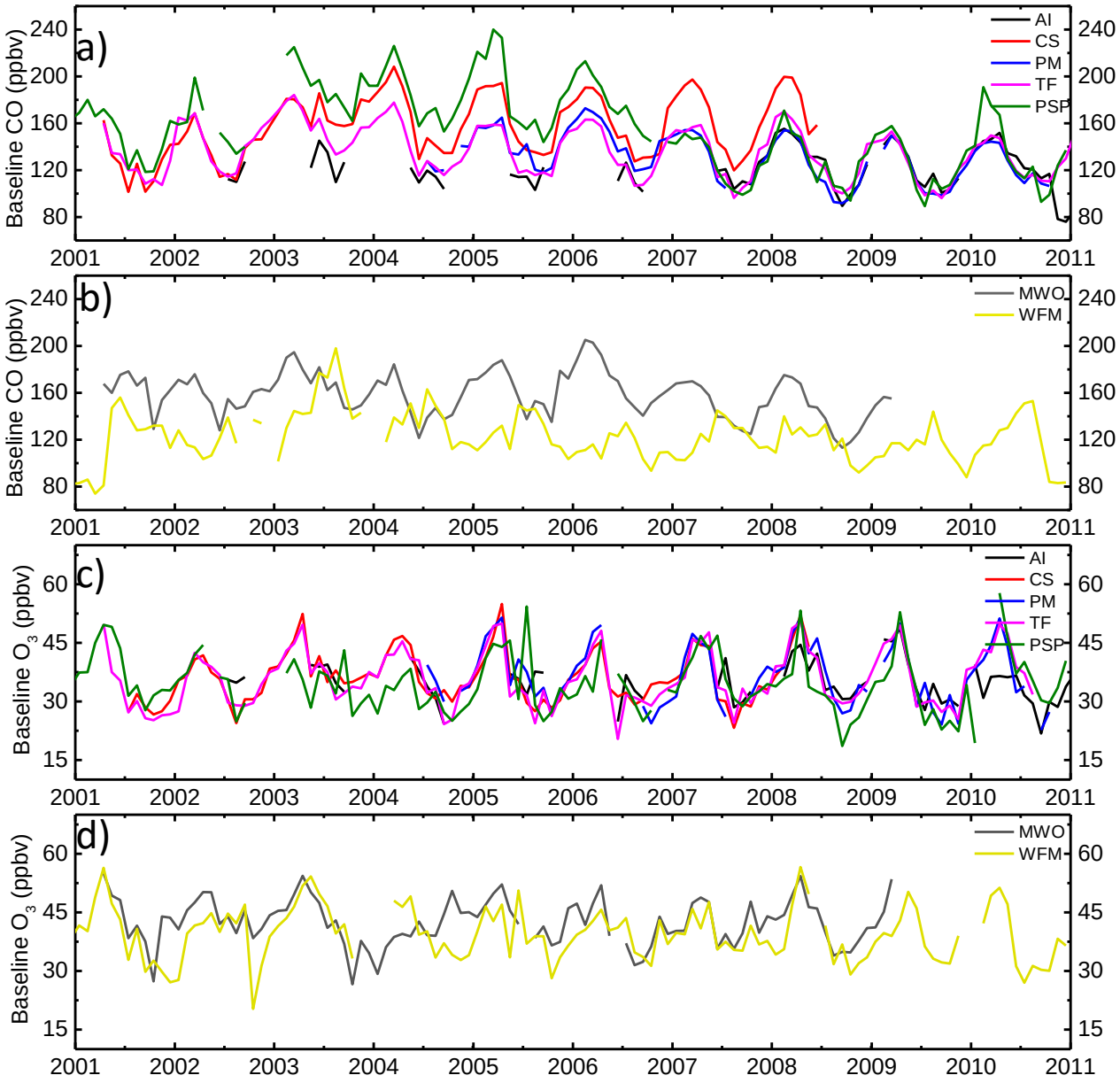

Fig. 2. Monthly baseline CO (ppbv) at (a) AI, CS~~, MWO~~, PM, ~~and~~ TF, and PSP. and (b) MWO and WFM~~PSP~~. Monthly baseline O_3 (ppbv) at (c) AI, CS~~, MWO~~, PM~~, and~~ TF, and PSP, and (d) MWO and WFM~~PSP~~.

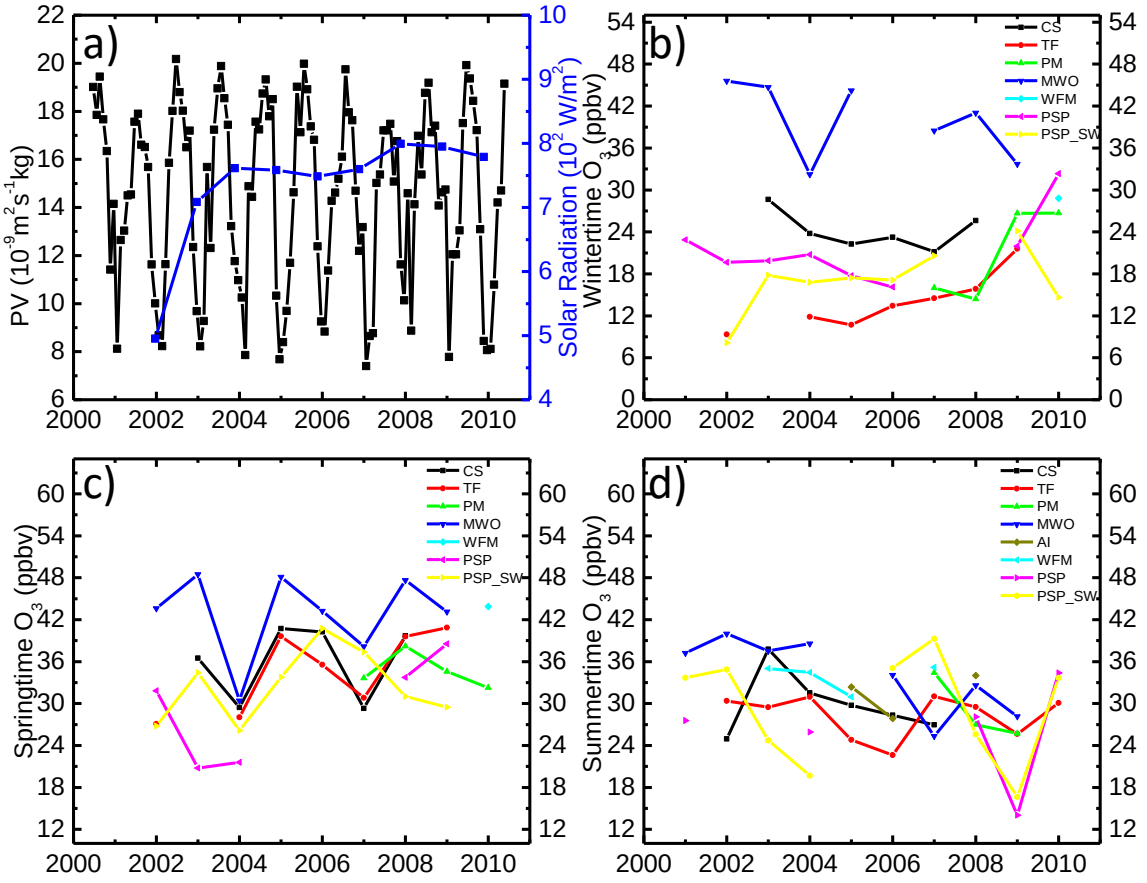

Fig. 3. (a) Time series of monthly PV (10^{-9} m^2 s^{-1} kg) at 350 K over the study region (40ºN – 45ºN, 70ºW – 77.5ºW, indicated with dashed box in Fig. 1) and averaged daily maximum solar radiation flux at TF in spring (March, April, and May) . Seasonal 10th percentile mixing ratios of O_3 with wind from the directions aligned with the urban corridor in (b) winter, (c) spring, and (d) summer. Specifically, the wind directions selected for AI: 157.5° - 202.5°; CS: 157.5° - 202.5°; MWO: 157.5° - 202.5°; PM: 112.5° - 157.5°; TF: 157.5° - 202.5°; WFM: 112.5° - 157.5°; PSP: 67.5° - 112.5°. In addition, seasonal 10th percentile mixing ratios of O_3 at PSP with wind from the directions aligned with the Ohio River Valley was calculate as PSP_SW (202.5° - 247.5 °) in (b), (c), and (d).

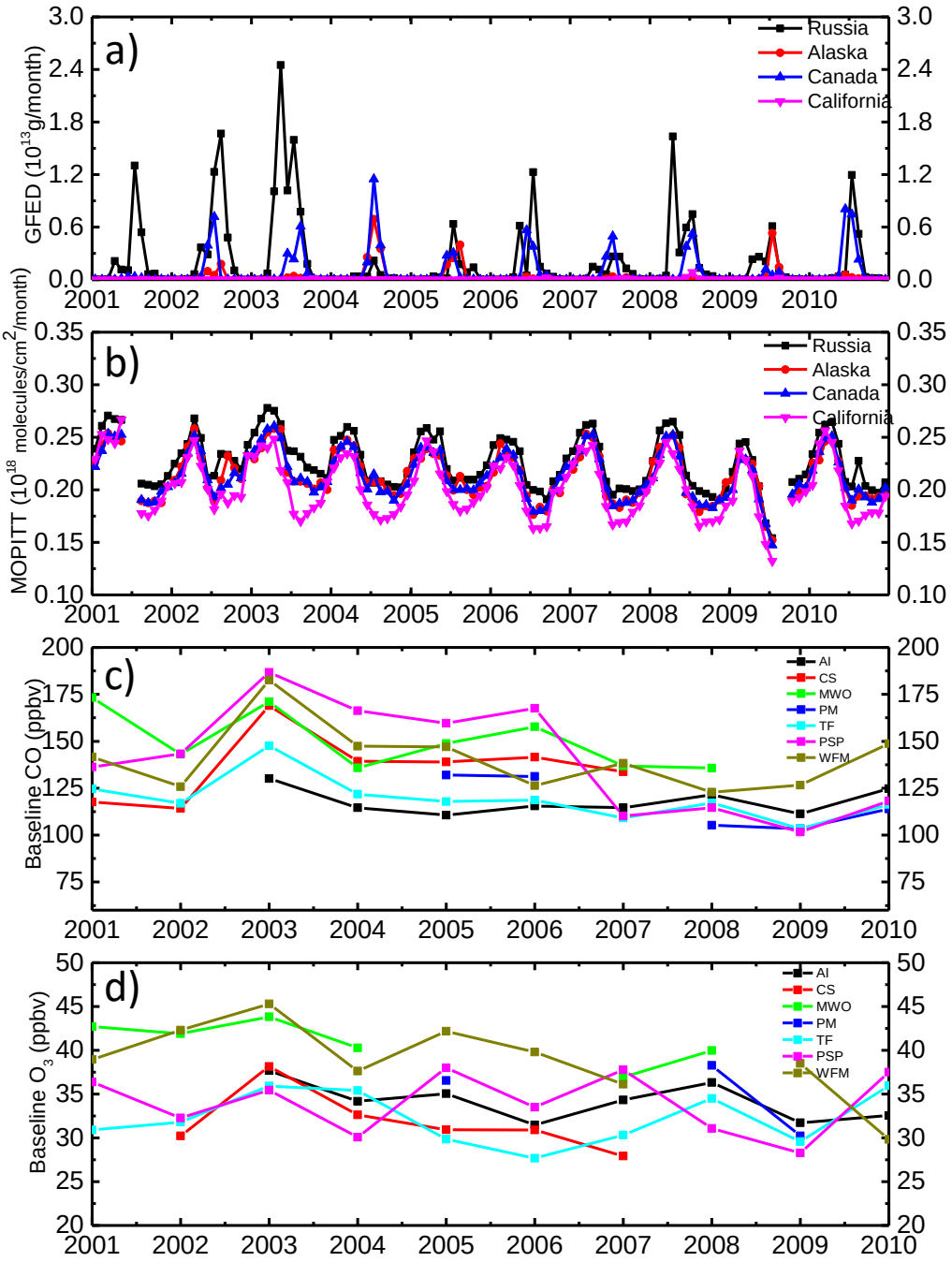

Fig. 4. (a) CO emissions from biomass burning based on GFED dataset. (b) Total CO columns based on MOPITT retrievals over Russia (black), Alaska (red), Canada (blue), and California (magenta). Summertime averaged baseline (c) CO and (d) O_3 at each site.

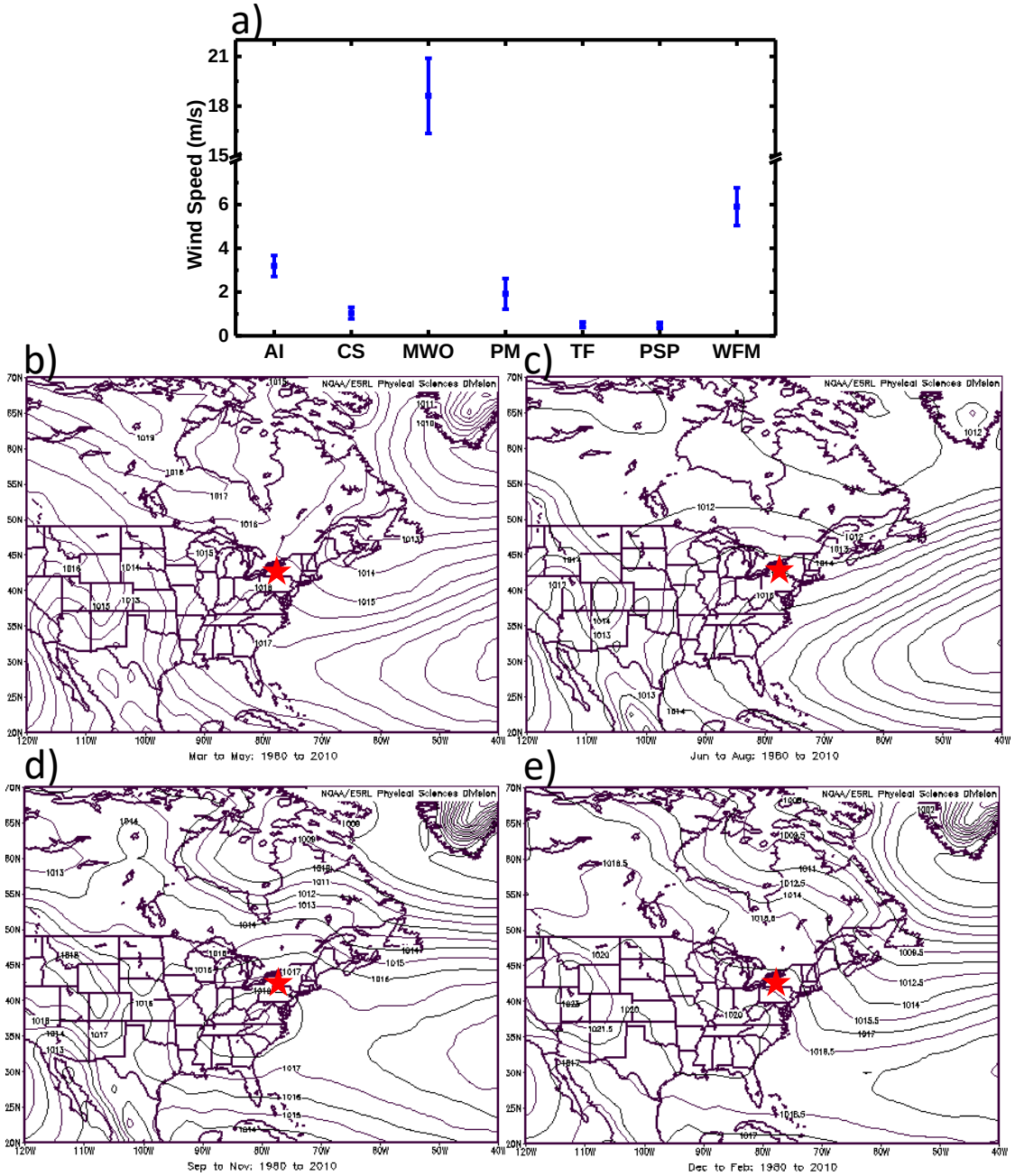

Fig. 5. (a) Annual surface wind speed with yearly variation at each site over summer 2001 – 2010. Northeast U.S. sea surface pressure (hPa) in (b) spring, (c) summer, (d) fall, and (e) winter. Red stars indicate the location of PSP.

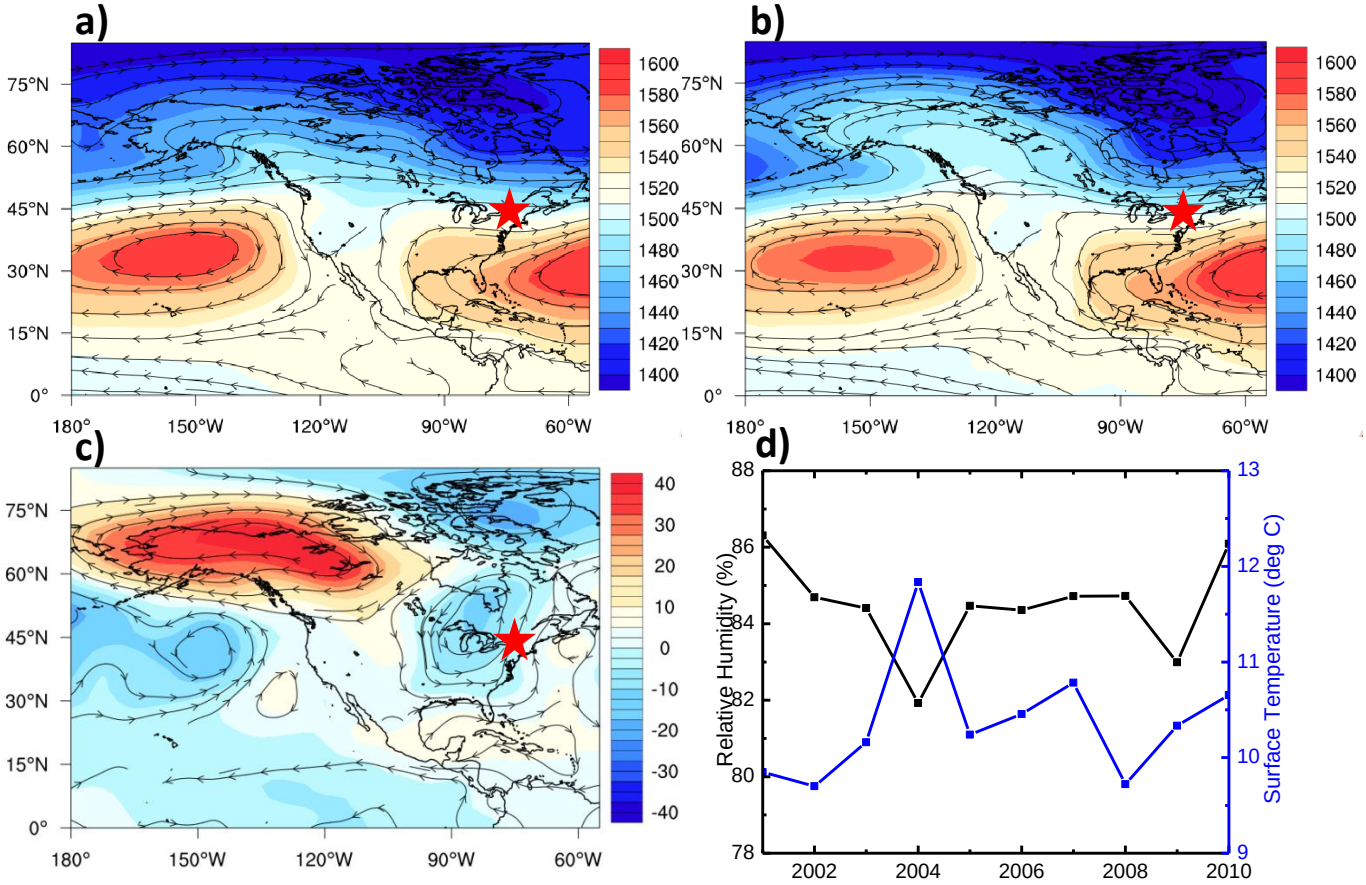

Fig. 6. Geopotential height at the 850 hPa pressure level during summer in (a) 2001-2010 (b) 2004. (c) The difference of geopotential height at 850 hPa between summer 2004 and the 10-year average. (d) The annual surface temperature and relative humidity over Alaska and southwestern Canada (55°N – 70°N, 110°W – 160°W) over summer 2001 – 2010. Red stars indicated the area of the study sites. (Source: NCEP/NCAR reanalysis)

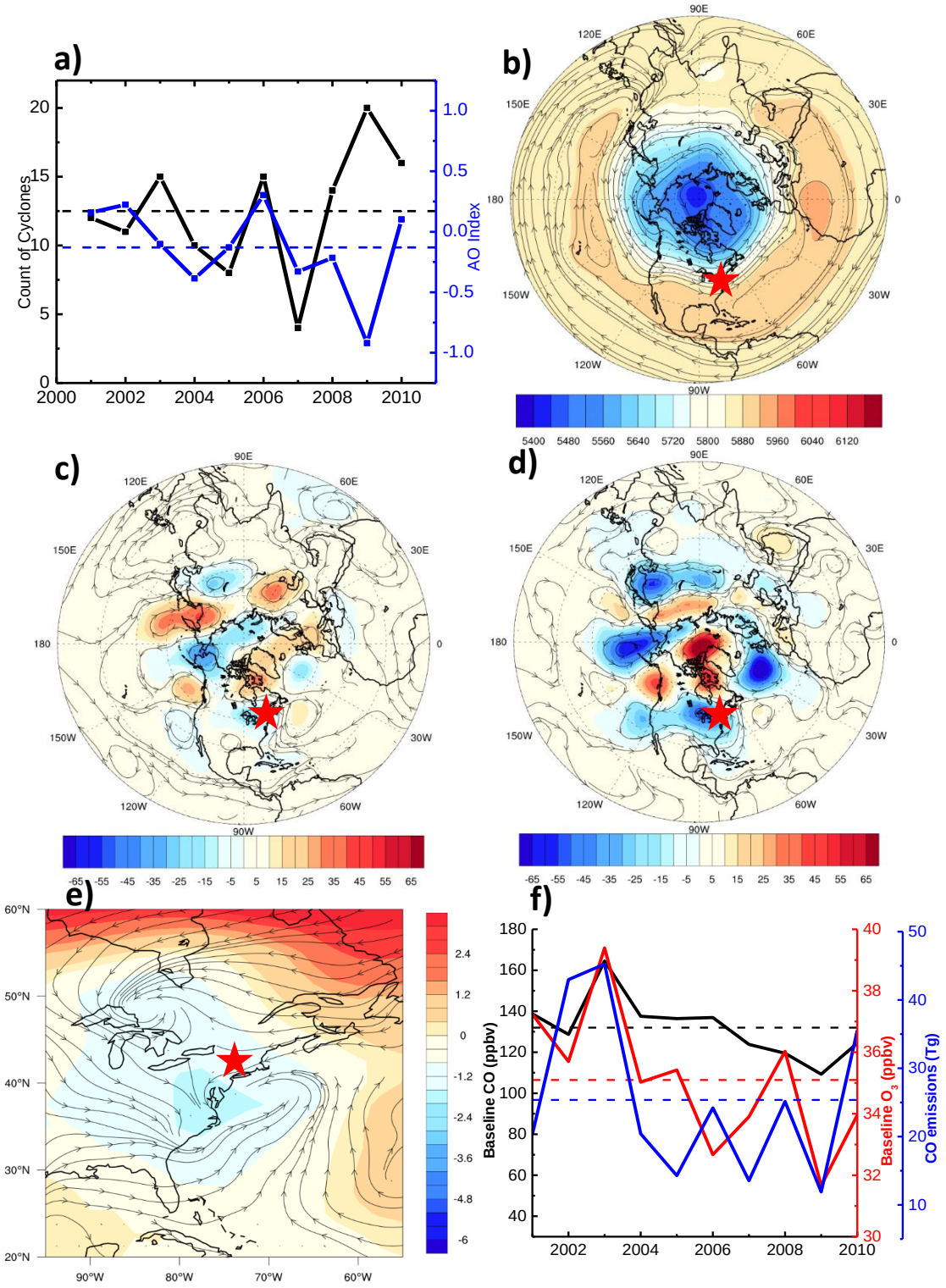

Fig. 7. (a) Counts of cyclones in the Northeast U.S. (black) and the AO index (blue) in summer. (b) Geopotential height at 500 hPa from the NCEP/NCAR reanalysis data during summer 2001 – 2010. (c) The difference of geopotential height at 500 hPa between years with strong (2003, 2006, 2008, 2009, and 2010) and weak (2001, 2002, 2004, 2005, and 2007) cyclone activities. (d) The difference of geopotential height at 500 hPa between summer 2009 and the 10-year means. (e) The difference of sea level pressure between summer 2009 and the 10-year means. (f) Time series of summertime baseline CO (black) and baseline O_3 (red) averaged over all sevent sites, and Time series of CO emissions (blue) from wildfires in Russia and Canada. Dashlines indicate the 10-year means. Red stars indicate the area of the study sites.

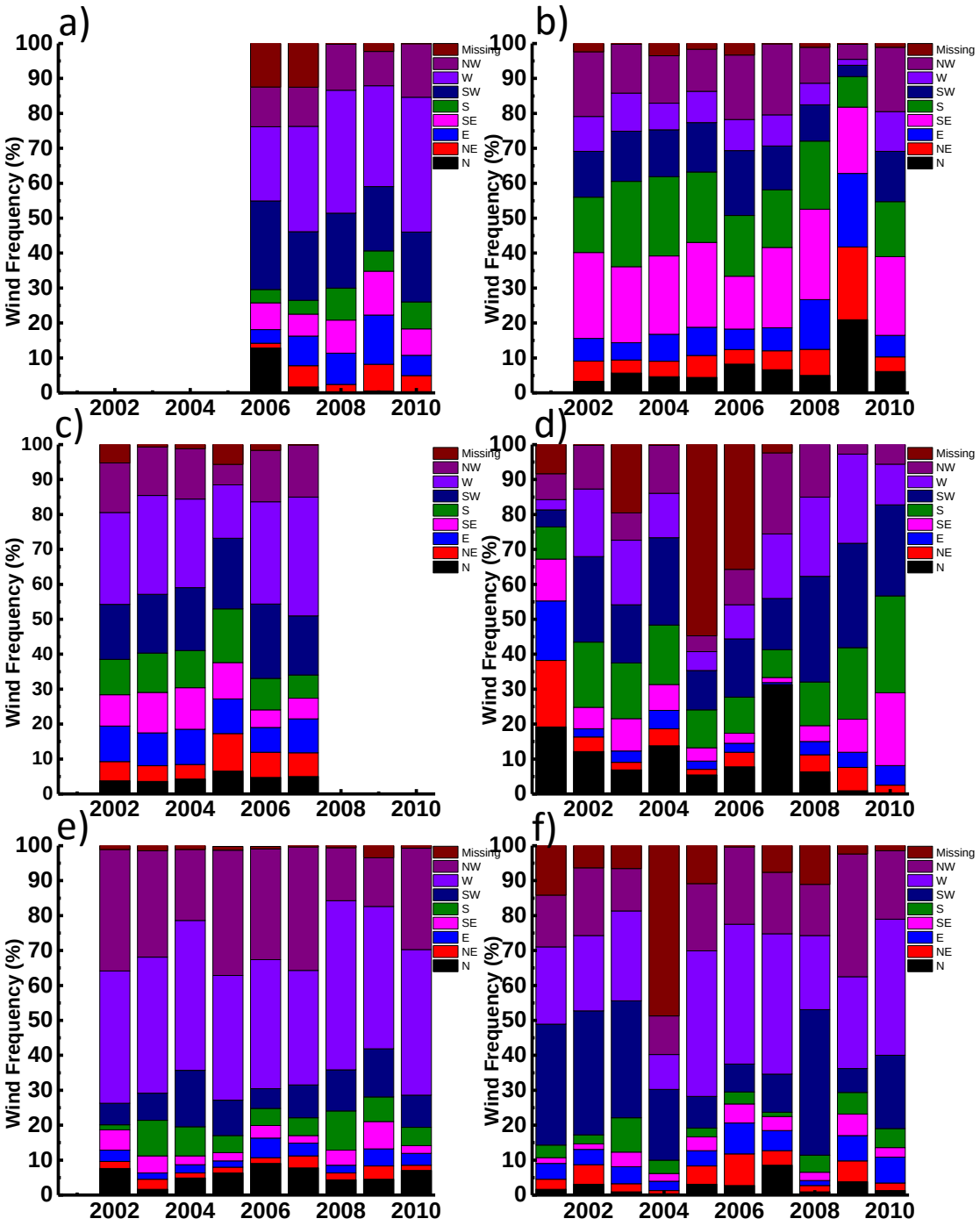

Fig. 8. Wind frequency in summer at (a) PM, (b) MWO, (c) CS, (d) WFM, (e) TF, (f) PSP. N:- 22.5° – 22.5°; NE: 22.5° – 67.5°; E: 67.5° – 112.5°; SE: 112.5° – 157.5°; S: 157.5° – 202.5°; SW: 202.5° – 247.5°; W: 247.5° – 337.5°; NW: 337.5° – -22.5°

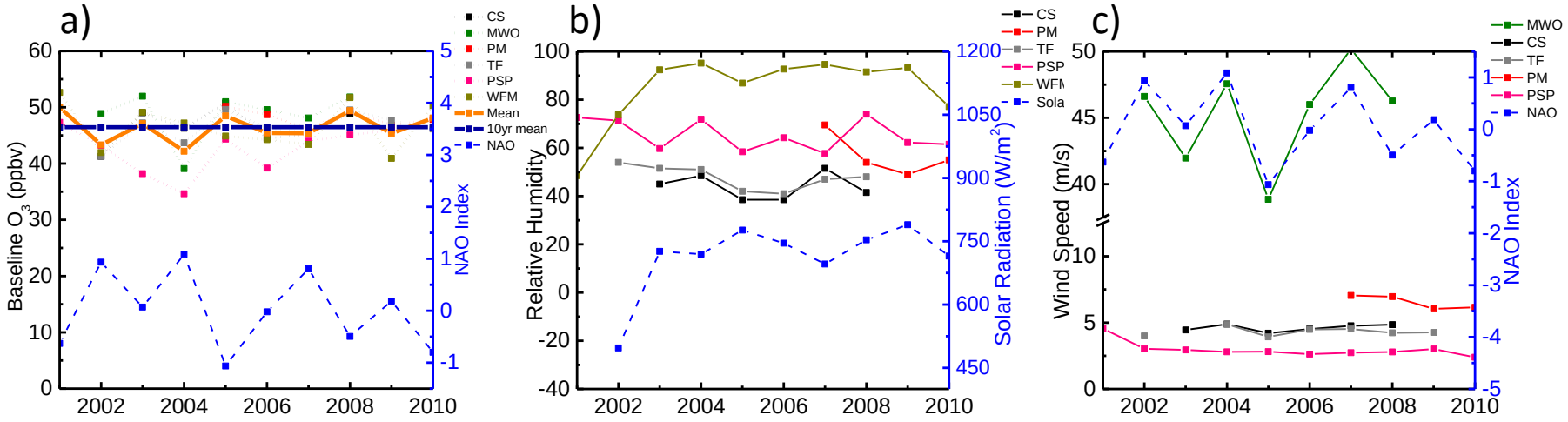

Fig. 9. (a) Baseline O_3 and the NAO index averaged in March and April. The thick orange line indicates the baseline O_3 averaged over the seven sites and the thick dark blue line indicates the mean value 46.5 ppbv over 2001 – 2010. (b) Averaged daytime (18:00 – 24:00 UT) relative humidity and daily maximum solar radiation flux at TF in March and April. (c) Averaged wind speed (> 2 m s^{-1}) from the west (247.5° – 337.5°) and the NAO index in March and April.

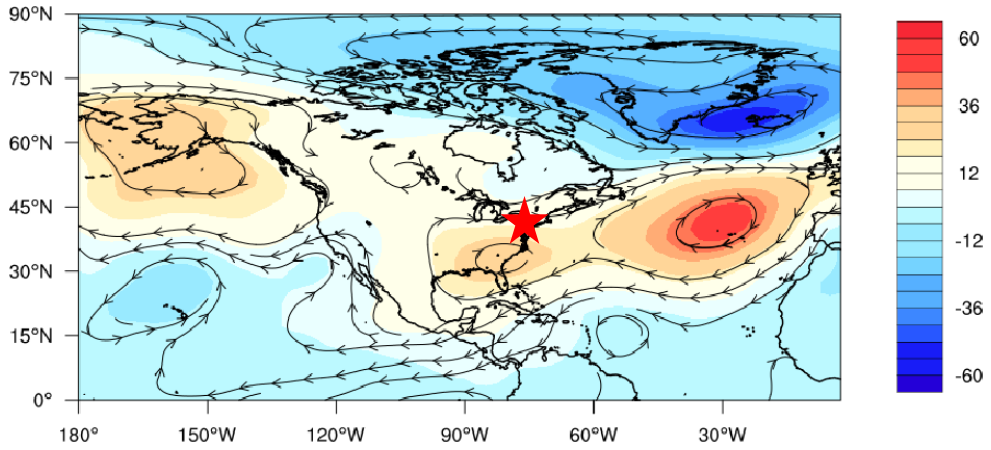

Fig. 10. The difference of geopotential height (m) and streamlines at 850-hPa between the low O_3 years (2002, 2004, 2006, 2007, and 2009) and high O_3 years (2001, 2003, 2005, 2008, and 2010). The red star indicates the area including the study sites.

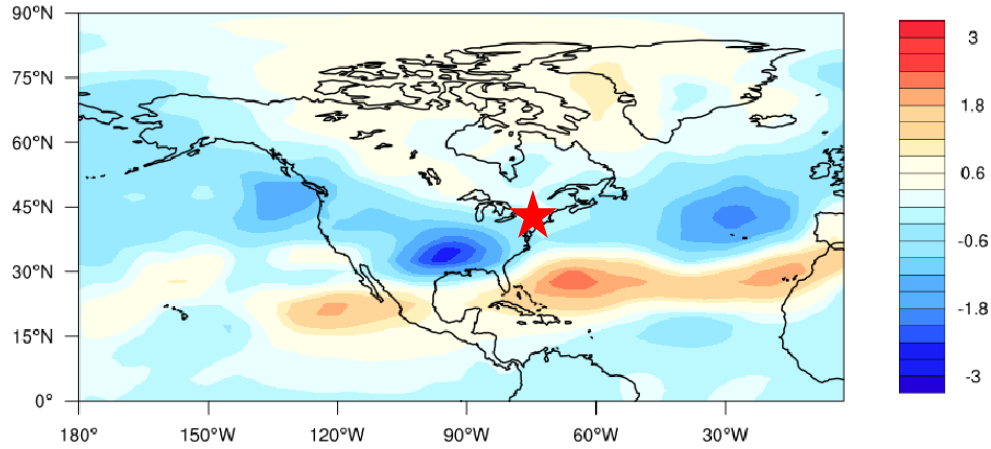

Fig. 11. Same as Fig. 10 except that the difference of PV (10^{-9} m^2 s^{-1} kg) at 350 K is shown.