Reactive Nitrogen, Ozone and Ozone production in the Arctic Troposphere and the Impact of Stratosphere-Troposphere Exchange

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Abstract

We analyze the aircraft observations obtained during the Arctic Research of the Composition of the Troposphere from Aircraft and Satellite (ARCTAS) mission together with the GEOS-5 CO simulation to examine O₃ and NOₓ in the Arctic and sub-Arctic region and their source attribution. Using a number of marker tracers and their probability density distributions, we distinguish various air masses from the background troposphere and examine their contribution to NOₓ, O₃, and O₃ production in the Arctic troposphere. The background Arctic troposphere has mean O₃ of ~ 60 ppbv and NOₓ of ~ 25 pptv throughout spring and summer with CO decreases from ~ 145 ppbv in spring to ~ 100 ppbv in summer. These observed CO, NOₓ and O₃ mixing ratios are not notably different from the values measured during the 1988 ABLE-3A and the 2002 TOPSE field campaigns despite the significant changes in the past two decades in processes that could have changed the Arctic tropospheric composition. Air masses associated with stratosphere-troposphere exchange are present throughout the mid and upper troposphere during spring and summer. These air masses with mean O₃ concentration of 140-160 ppbv are the most important direct sources of O₃ in the Arctic troposphere. In addition, air of stratospheric origin is the only notable driver of net O₃ formation in the Arctic due to its sustainable high NOₓ (75 pptv in spring and 110 pptv in summer) and NOᵧ (~800 pptv in spring and ~1100 pptv in summer) levels. The ARCTAS measurements present observational evidence suggesting significant conversion of nitrogen from HNO₃ to NOₓ and then to PAN (a net formation of ~120 pptv PAN) in summer when air of stratospheric origin is mixed with tropospheric background during stratosphere-to-troposphere transport. These findings imply that an adequate representation of stratospheric O₃ and NOₓ input are essential in accurately simulating O₃ and NOₓ photochemistry as well as the atmospheric budget of PAN in tropospheric chemistry transport models of the Arctic. Anthropogenic and biomass burning pollution plumes observed during ARCTAS show highly elevated hydrocarbons and NOₓ (mostly in the form of NOₓ and PAN), but do not contribute significantly to O₃ in the Arctic troposphere except in some of the aged biomass burning plumes sampled during spring. Convection and/or lightning influences are negligible sources of O₃ in the Arctic troposphere but can have significant impacts in the upper troposphere in the continental sub-Arctic during summer.
1. Introduction

Tropospheric ozone ($O_3$) is important as a surface pollutant affecting air quality and is also a greenhouse gas. The Arctic has been warming at twice the global average rate over the past century (IPCC, 2007). While increases in long-lived greenhouse gases dominate Arctic warming, $O_3$ and other short-lived pollutants (e.g. aerosols) could also play an important role (Law and Stohl, 2007; Shindell, 2007; Quinn et al., 2007). Changes in local tropospheric $O_3$ affect Arctic climate by altering local radiation fluxes with maximum impact near the tropopause (Hansen et al., 1997). A recent modeling study suggested that an increase in tropospheric $O_3$, caused by increases in anthropogenic emissions, could have contributed about 0.3°C surface temperature increase on an annual average and about 0.4°C - 0.5°C during winter and spring to the 20th-century Arctic warming (Shindell et al., 2006). The impact of possible increases in boreal forest fire emissions or changes in the stratospheric $O_3$ flux is not yet well quantified.

Ozone is produced locally in the Arctic troposphere from its precursors (carbon monoxide (CO), hydrocarbons, nitrogen oxides ($NO_x$)) emitted from anthropogenic and biomass burning sources in adjacent continents (e.g. Penkett and Brice, 1986; Wofsy et al., 1992; Beine et al., 1997). Additional potential sources of $O_3$ in the Arctic troposphere include transport of remote $O_3$ from the lower latitudes (Shindell et al., 2008) as well as transport from the stratosphere (Dibb et al., 2003; Allen et al., 2003). Stratospheric air contains high $NO_x$ and nitric acid (HNO$_3$) and is also an important source of $NO_x$ when injected into the Arctic troposphere (Wofsy et al., 1992; Levy et al., 1999; Law and Stohl, 2007; Liang et al., 2009). Increase in $NO_x$ due to stratospheric intrusion is the driving mechanism that leads to enhanced $O_3$ production in the Arctic upper troposphere (Liang et al., 2009). A better quantification of the contribution of various anthropogenic and natural sources to $O_3$ in the Arctic has important implications for understanding the temporal variation and radiative impact of $O_3$, and how the Arctic $O_3$ level may change as climate warms and the stratospheric $O_3$ layer recovers.

The NASA Arctic Research of the Composition of the Troposphere from Aircraft and Satellite (ARCTAS) mission was conducted in April and June-July 2008 (Jacob et al., 2010). Its goal was to better understand the factors driving the changes in Arctic atmospheric composition and climate. The extensive and detailed measurements of $O_3$ and reactive nitrogen ($NO_y$) species provided an unprecedented opportunity to examine the photochemistry of $O_3$ and $NO_y$, and their sources in the Arctic. In this paper, we will use airborne observations obtained onboard the NASA DC-8 aircraft during ARCTAS and the GEOS-5 model simulated CO to examine $O_3$ and $NO_y$ in the Arctic and sub-Arctic region and their source attribution. This analysis is then used to address the implications of ARCTAS measurements to our understanding of the relative contribution of different sources to $O_3$ and $NO_y$ in the Arctic. Section 2 describes the observations and model used in this study. Section 3 compares the CO observations collected during ARCTAS with the model simulated CO to examine the representativeness of the ARCTAS measurements to the general characteristics of the Arctic troposphere. This helps to extrapolate the findings from the ARCTAS to achieve a better understanding of the general characteristics of the Arctic troposphere. We use a set of marker tracers to identify various air masses sampled during ARCTAS and examine their chemical composition, as described in section 4. In Sections 5 and 6, we examine $NO_y$, $O_3$, $O_3$ production within individual air masses sampled during ARCTAS to identify sources of $O_3$ in the Arctic. Conclusions are presented in Section 7.

2. Observations and Model

2.1 Observations
The NASA ARCTAS mission had two phases. The spring deployment (ARCTAS-A), based in Fairbanks, Alaska, involved nine flights by the NASA DC-8 aircraft between 1 April and 21 April 2008. The summer deployment (ARCTAS-B) took place between 26 June and 14 July 2008 (nine flights) and was operated from a base in Cold Lake, Canada. Figure 1 shows the geographical distribution of flight tracks of the DC-8 aircraft during ARCTAS. Here we use measurements obtained north of 50°N. During the spring phase, the majority of the measurements are between 60°N-90°N. Measurements made during the summer phase were mainly in the sub-Arctic between 50°N-70°N.

Observations obtained onboard the DC-8 aircraft include a comprehensive suite of measurements of O₃, HOₓ (OH+HO₂), NOₓ, as well as NOₓ reservoir species, hydrocarbons, halocarbons, aerosols (Jacob et al., 2010). Segregation between various air masses relies on the availability of simultaneous measurements of the marker tracers, e.g. CO and acetonitrile (CH₃CN) for combustion plumes and chlorofluoro carbons (CFCs) for stratospheric air. A detailed list of the species used in the study and the associated instrument specifications is presented in Table 1. Multiple merge files (1-sec, 10-sec, 60-sec) were created for the ARCTAS measurements. Here, we rely on the 60-sec merge. Although many species are available at higher frequency, measurements crucial to this analysis including halocarbons and acetylene (C₂H₂) from the Whole Air Sampler – Gas Chromatography are obtained every four minutes.

2.2 GEOS-5 CO

A CO simulation was conducted for the ARCTAS period using the GEOS-5 Atmospheric Data Assimilation System (GEOS-5 ADAS) with the Modern Era Retrospective-analysis for Research and Applications (MERRA) tag (http://geos5.org/wiki/index.php?title=GEOS-5_Configuration_for_ARCTAS). Instantaneous CO is output on a 0.5° latitude by 0.67° longitude for 72 eta layers from the surface to 0.01 hPa, every 6 hours. Sources of CO include fossil fuel, biofuel, and biomass burning emissions as well as production from methane (CH₄) and non-methane hydrocarbon (NMHC) oxidation. Fossil fuel emissions are based on EDGAR 2000 with updated emissions from EPA/NEI99 for the continental USA, EMEP for Europe, BRAVE for Northern Mexico, the Zhang et al. (2009) inventory for SEA and China. Biofuel emissions are from Yevich et al. (2003). For biomass burning emissions, we use the Quick Fire Emission Dataset (QFED), the near-real time biomass burning emission system from the NASA Global Modeling and Assimilation Office. The QFED emissions are based on satellite retrieved fire hot spot detections from the Moderate Resolution Imaging Spectroradiometer (MODIS) fire product and scaled to yield a global emission that matches the Global Fire Emission Database (van der Werf et al., 2006). To account for production of CO from co-emitted NMHC, we apply scale factors to the direct emission sources (1.20 for fossil fuel, 1.19 for biofuel, and 1.11 for biomass burning) following Duncan et al. (2007b). We calculate CO produced from CH₄ oxidation using monthly mean CH₄ fields compiled from the long-term Global Monitoring Division (GMD) GLOBALVIEW-CH₄ observations and a yield of 1.0 of CO from CH₄ oxidation (Bian et al., 2007). Oxidation of CO is calculated using previously archived monthly OH fields from the Global Modeling Initiation (GMI) combo chemistry simulation (Duncan et al., 2007a). In addition to total CO, we also use multiple tagged tracers to track CO from anthropogenic and biomass burning pollutions emitted in different regions in the Northern Hemisphere tag (http://geos5.org/wiki/index.php?title=GEOS-5_Configuration_for_ARCTAS). We present the sum of anthropogenic pollution from North America, Europe and Asia and the sum of N. Hemispheric boreal and non-boreal biomass emissions in this study.
3. **ARCTAS in the context of Arctic Spring and Summer 2008**

While airborne field missions provide an extensive set of trace gas measurements over vast spatial regions, the flight plans are usually designed to target pollution plumes and thus biased towards these plumes. Thus, a simple average of these aircraft measurements may provide a biased view that is not representative of the general atmospheric composition. In this section, we i) evaluate the GEOS-5 simulated CO, and ii) examine the representativeness of the ARCTAS sampling to the general characteristics of the Arctic troposphere. Carbon monoxide is a commonly used tracer for combustion and atmospheric transport. Acetylene and CO have common combustion sources and are removed by reaction with OH in the atmosphere with different lifetime, which is about two weeks for \( C_2H_2 \) and two months for CO (e.g. Blake et al., 2003; Wofsy et al., 1992). The \( C_2H_2/CO \) ratio can be used as a tracer of pollution and it offers additional valuable information on the time since emission of pollutants and the extent of mixing with background air (e.g. Smyth et al, 1996; Xiao et al., 2007).

Figure 2 shows an overall comparison of the GEOS-5 simulated CO and observed CO during ARCTAS. The model results are sampled at the closest grid and time and interpolated vertically to the aircraft pressure level. Both the simulated CO and observed CO are averaged in 1-km vertical bins from the surface to 12 km. The model reproduces well the observed vertical profile (Figure 2a) and variability (\( r=0.69 \), Figure 2b) during ARCTAS-A with a systematic low bias of 15-20 ppbv in the middle and lower troposphere. The contribution from anthropogenic pollution to total CO is ~60% (80 ppbv) and decreases with altitude. Biomass burning emission accounts for ~30% (40 ppbv) of total CO and its contribution remains relatively constant throughout the troposphere. The vertical profile of CO during summer shows a distinctive peak at the surface associated with active boreal forest fires in Canada (Alvarado et al., 2010) and a secondary peak at about 10 km due to enhanced convective outflow of anthropogenic pollution (Figure 2c), mostly from Asia (Fisher et al., 2010). The model well captures the observed vertical gradient of CO, but the simulated CO is less correlated with observations (\( r=0.49 \)) and shows a more pronounced low bias (-37 ppbv) compared to spring (-25 ppbv). A significant part of the model low bias in summer is due to the inability of model to correctly represent the intensity and location of the highly localized biomass burning plumes with significantly elevated CO. The systematic low bias in the mean model CO throughout spring and summer is likely associated with too high values in the archived GMI OH fields. This low bias was previously noted in Duncan et al. (2007a) when comparing GMI simulated CO with the NOAA GMD surface observations. Although our mean tropospheric OH (0.98x10^6 molec/cm^3) and the calculated methyl chloroform (CH_3CCl_3) lifetime (6.1 y) are similar to observation-based values reported by Prinn et al. (2005) and Spivakovsky et al. (2000) (1.16x10^6 molec/cm^3 for OH concentrations, 5.7-6.0 y for CH_3CCl_3 lifetime), the lifetime of CH_3CCl_3 is heavily weighted towards the tropical lower troposphere and offers little information on the quality of the simulated OH elsewhere (Lawrence et al., 2001; Duncan et al., 2007a).

Figure 3 shows the probability density function (PDF) of CO for ARCTAS-A. The observed CO sampled by DC8 (CO_{ObsDC8}, red lines) displays a unimodal distribution in the lower and mid troposphere during spring with peaks at 160 ppbv and 145 ppbv, respectively. In the upper troposphere/lower stratosphere (UT/LS), CO_{ObsDC8} distribution is bimodal, with one peak at 125 ppbv and a secondary peak at ~50 ppbv representing tropospheric and stratospheric air masses, respectively. We examine the PDF of model CO along DC-8 flight track (CO_{ModDC8}, black lines). To facilitate comparison with the observed PDF, a corrected PDF of CO_{ModDC8} (black line-filled shading) is shown by adding a uniform +25 ppbv to account for the systematic low bias. The value
of +25 ppbv is determined by taking the difference between the mean CO\textsubscript{Obs} and the mean CO\textsubscript{Mod} in tropospheric air mass. The corrected CO\textsubscript{Mod} distribution agrees with the observations in the lower and mid-troposphere, and is slightly larger than observations in the UT/LS. The absence of a distinctive peak at ~ 50 ppbv in CO\textsubscript{Mod} in the UT/LS likely implies that there are biases in stratosphere-troposphere exchange in the high latitude tropopause region in the GEOS-5 MERRA.

The PDF of CO\textsubscript{Obs} (red lines) during ARCTAS-B, shown in Figure 4, displays multiple peaks in the troposphere. The primary peak around 100 ppbv (90-120 ppbv) represents the background atmosphere and the two peaks between 120-160 ppbv (present in the upper and lower troposphere) and > 160 ppbv (present in the mid- and upper troposphere) are associated with fresh pollution. Acetonitrile is typically used as a tracer for biomass burning plumes (Lobert et al., 1990; Holzinger et al., 2001). The mean concentration of CH\textsubscript{3}CN is 200 pptv for air masses with CO between 120-160 ppbv and 520 pptv for those with CO > 160 ppbv. This suggests that the measurements between 120-160 ppbv are mostly associated with anthropogenic plumes and those have CO > 160 ppbv are mostly tied to biomass burning plumes. The fact that the combustion peaks are well separated from the background suggests these are fresh pollution plumes that have not yet mixed into the background. Again to facilitate visual comparison, we add a correction of +15 ppbv to the CO\textsubscript{Mod} which gives the best line-up between the corrected CO\textsubscript{Mod} and CO\textsubscript{Obs}. Note this +15 ppbv correction is only ~40% of the summertime model mean bias (37 ppbv) as the majority of the bias is due to differences between the model and observation in a few biomass burning plumes that have very high CO levels. The corrected CO\textsubscript{Mod} distribution (black line-filled shading) reproduces the skewness and the individual peaks in the observations. Despite the systematic bias due to OH, the fact that GEOS-5 produces the variation and distribution of the observed CO suggests that the model presents a realistic representation of the transport of pollution plumes in the Arctic troposphere as well as their mixing with the background air.

In Figures 2 and 4 we also compare CO\textsubscript{Mod} with the simulated GEOS-5 CO in the mean atmosphere (CO\textsubscript{ModMean}, blue shades), define as the monthly averaged CO between 50°N-90°N and 130°W-180°W, in April and July 2008 to investigate the representativeness of the ARCTAS measurements. The peak and spread of the PDF of CO\textsubscript{Mod} (Figure 3) during April is very similar to that of CO\textsubscript{ModMean} in the middle and lower troposphere. Sampling in the UT/LS is biased towards the troposphere with less sampling of lower stratospheric air mass. This suggests in general the sampling during ARCTAS-A reflects well the mean composition of Arctic troposphere during spring. A similar comparison in July (Figure 4) suggests that the sampling during ARCTAS-B, on the contrary, is highly skewed towards combustion plumes at all altitudes, particularly in the lower troposphere.

We now examine the C\textsubscript{2}H\textsubscript{2}/CO ratio during ARCTAS as an additional marker for further examination of the age of pollution plumes and their mixing with background (Figure 5). In general, the C\textsubscript{2}H\textsubscript{2}/CO ratio is highly correlated with CO with \( r = 0.81 \) in spring and \( r = 0.69 \) in summer. Similar to CO (Figure 3), the PDF of the C\textsubscript{2}H\textsubscript{2}/CO ratio during spring displays a near-normal unimodal distribution (Figure 5a). The extended left tail is partly associated with aged stratospheric air with low C\textsubscript{2}H\textsubscript{2}/CO values and partly due to the reaction of C\textsubscript{2}H\textsubscript{2} with bromine in the marine boundary layer during bromine explosion events (Jobson et al., 1994). Depletion of C\textsubscript{2}H\textsubscript{2} has been previously observed in the Arctic in spring during many bromine explosion events (e.g. Jobson et al., 1994; Toyota et al., 2004; Ridley et al., 2007). During summer, the PDF of C\textsubscript{2}H\textsubscript{2}/CO ratio displays a clear bimodal distribution with one peak at ~ 0.7-0.8 pptv/ppbv corresponding to the aged background air and another peak at ~ 1.2 pptv/ppbv that is associated
with fresh anthropogenic and biomass burning pollutions (Figure 5b). The distributions of the 
C\textsubscript{2}H\textsubscript{2}/CO ratio and CO are consistent, both supporting the interpretation that the measurements obtained during ARCTAS-A are representative of a well-mixed Arctic troposphere due to slow atmospheric transport, in contrast to intensive sampling of fresh anthropogenic and biomass burning plumes that have not experienced much mixing with the background as in ARCTAS-B.

4. Air mass observed during ARCTAS
4.1 Air mass identification

We use a comprehensive set of tracers to characterize air masses sampled by the DC-8 aircraft during ARCTAS. The detailed criteria applied to define each type of air mass are listed in Table 2. Note that the thresholds of marker gases chosen to segregate air masses of different origin are highly objective and can vary significantly depending on season, location, and the question of interest. While we choose some criteria based on previous literature (O\textsubscript{3} > 100 ppbv for air of stratospheric origin) and the PDF distribution of CO (section 3) for combustion plumes, we heavily rely on tracer-tracer correlations for optimal segregation between different air masses (supplementary Figures 7, 8, S1 and S2). We found that the CO-NO\textsubscript{y}, CO-CO\textsubscript{2} and CO-CH\textsubscript{4} correlations are particularly useful in determining the threshold levels of markers for distinguishing air in the stratosphere, air associated with recent STE, biomass burning and anthropogenic plumes.

We use CO and CH\textsubscript{3}CN to distinguish anthropogenic and biomass burning pollution plumes. Since pollution plumes are not well separated from the background during spring (section 3), we use the highest quartile of CO (> 160 ppbv) to define pollution plumes. Within the pollution plumes, air masses with CH\textsubscript{3}CN > 145 pptv are identified as biomass burning plumes and the remaining as anthropogenic pollution plumes. During summer, air masses with CO > 120 ppbv are defined as combustion plumes (Table 2). We further use CO > 160 ppbv and CH\textsubscript{3}CN > 320 pptv to separate biomass burning air masses from anthropogenic plumes. The thresholds of CH\textsubscript{3}CN ~ 145 pptv for ARCTAS-A and ~ 320 pptv for ARCTAS-B are chosen for optimal segregation between the biomass burning and anthropogenic pollutions based on the CO\textsubscript{2}/CO, CH\textsubscript{4}/CO, and C\textsubscript{2}H\textsubscript{6}/CO ratios (Table 2), which differ in the two type of air masses (supplementary Figures S1 and S2).

Air in the stratosphere is enriched in O\textsubscript{3} and depleted in surface emitted pollutants such as the long-lived CFCs (lifetime ~ 45-100 years) as well as the short-lived CO (lifetime ~ two months). Stratospheric air can enter the troposphere through rapid synoptic eddy exchange activities, e.g. tropopause folds, or slow global-scale diabatic descent (Holton et al., 1995). The stratosphere-to-troposphere transport time ranges between a few days during rapid tropopause folding events that intrude deeply into the troposphere to the order of a month for shallow stratosphere-troposphere-exchange (STE) intrusions followed by subsequent slow diabatic descent. The difference in transport time can lead to significantly different levels of trace gases, in particular the short-lived species such as O\textsubscript{3}, HNO\textsubscript{3}, Be-7 (Liang et al., 2009). We use the combination of a short-lived tracer, O\textsubscript{3} (> 100 ppbv), and a long-lived tracer, CFC-113 (lowest quartile, < 78 pptv) to identify air of stratospheric origin. We choose CFC-113 over the other two more common CFCs, CFC-11 and CFC-12. This is because emission of CFC-113 has significantly reduced since year 2000 (Liang et al., 2008), due to the phase-out required by Montreal protocol. Therefore low CFC-113, together with high O\textsubscript{3}, is a better marker to distinguish air transported from the stratosphere. We apply an additional criterion, CO < 160 ppbv in spring (< 120 ppbv in summer) to exclude any samples that have mixed to some extent with fresh combustion plumes. We also use CO levels to distinguish the DC-8 sampled air that is of stratospheric-origin but has already penetrated into the troposphere through STE events (CO > 80 ppbv and 50 ppbv in spring and summer, respectively) from the air
that still resides in the lowermost stratosphere (Table 2). This is because air of stratospheric origin can have very different \( \text{NO}_y \) partitioning and photochemical properties, e.g. \( \text{O}_3 \) production rates, when it enters the troposphere and mixes with the tropospheric background, compared to air remains in the stratosphere. Note that the use of \( \text{O}_3 > 100 \text{ ppbv} \) for \( \text{STE} \) air masses is a stringent criterion that distinguishes only the relatively fresh \( \text{STE} \) events from the background atmosphere.

The DC-8 aircraft also encountered a few deep convective events during ARCTAS-B. Air masses that have recently experienced deep convection contain enhanced levels of \( \text{NO}_y \) associated with freshly-ventilated air from the boundary layer and/or lightning and are depleted in \( \text{HNO}_3 \) due to scavenging (e.g. Thompson et al., 1999; Liang et al., 2007). Thus we define air as convection/lightning influenced when \( \text{NO}_y \) exceeds 200 pptv and the \( \text{NO}_y/\text{HN0}_3 \) ratio exceeds > 1.2 pptv/pptv. During ARCTAS-A, six minutes (< 0.1% of a total ~4200 minutes) of DC-8 sampled air masses contain elevated \( \text{NO}_y \) (> 100 pptv) which were of neither anthropogenic/biomass burning nor stratospheric origin. Since deep convection is not common during the high latitude spring, these measurements are most likely tied to fresh aircraft exhaustions. We therefore exclude these air samples.

The remaining air masses are defined as background. Note that the DC-8 measurements in the Arctic marine boundary layer also include a few \( \text{O}_3 \) depletion events (\( \text{O}_3 < 30 \text{ ppbv} \)) during spring (Neuman et al., 2010) as well as local high \( \text{NO}_y \) plumes from coastal ship emissions in spring and Canadian power plants near Edmonton and Ft. McMurray in summer. We exclude these air samples in this analysis.

### 4.2 Air mass sampled during ARCTAS

A summary of the air mass composition sampled by the DC-8 aircraft during ARCTAS is shown in Table 3a (for ARCTAS-A) and Table 3b (for ARCTAS-B). About 58% of the spring measurements are from the background troposphere. Pollution plumes account for 21% of the observations, 17% for anthropogenic pollution and 4% for biomass burning plumes. Lowermost stratospheric air and fresh \( \text{STE} \) air account for 9% and 4% of the spring measurements, respectively. During ARCTAS-B, about 40% of the DC-8 sampled air is identified as fresh anthropogenic pollution and about 10% is attributed to fresh biomass burning plumes. However, as we discussed in section 3, the ARCTAS-B measurements are highly biased towards combustion plumes and thus the above fractionations are not representative of the general Arctic troposphere. Stratosphere air and \( \text{STE} \) together account for ~5% of the measurements. About 2% of the air sampled during ARCTAS-B was recently influenced by convection and/or lightning activities. Geographically, the majority of the convective and biomass burning plumes are located in the sub-Arctic between 50-70°N while anthropogenic and \( \text{STE} \) air masses are found throughout the Arctic and sub-Arctic (Figure 1).

The background Arctic troposphere during spring has mean \( \text{CO} \) concentration of ~145 ppbv, \( \text{O}_3 \) of ~60 ppbv, and \( \text{NO}_y \) of ~25 pptv (Table 3a). The background \( \text{CO} \) and the \( \text{C}_2\text{H}_2/\text{CO} \) ratio decrease with altitude (Figure 6ab, Table 3a), suggesting that pollution is mainly mixed into the background and trapped in the low altitudes and the atmospheric condition is stagnant. Background \( \text{O}_3 \) and \( \text{NO}_y \) remain relatively the same from spring to summer, but \( \text{CO} \) levels decrease to ~100 ppbv due to increased destruction by \( \text{OH} \) (Table 3b). Unlike spring, \( \text{CO} \) and the \( \text{C}_2\text{H}_2/\text{CO} \) ratio show little dependence on altitude, indicating efficient vertical mixing in summer. The \( \text{C}_2\text{H}_2/\text{CO} \) ratio shows a peak in the upper troposphere, a result of active ventilation of fresh pollution via deep convection.

The lowermost stratosphere, with low \( \text{CO} \) and \( \text{C}_2\text{H}_2/\text{CO} \) ratio, can reach as low as 6 km during spring, likely during low tropopause events (Figure 6ab). Significantly fewer samples of the lowermost stratospheric air (1%) were sampled during summer at > 10 km (Figure 6cd). This is
consistent with the seasonal growth of tropopause height from spring to summer. Frequent STE events have been observed throughout spring and summer. Air masses associated with fresh STE events are present at altitudes > 5 km (Figure 6). The STE air masses have higher CO and C$_2$H$_2$/CO ratio, compared to air in the lowermost stratosphere, reflecting mixing with tropospheric background air during stratosphere-to-troposphere transport.

The convective air masses observed during summer contain elevated CO (50% enhancement compared to background) and C$_2$H$_2$/CO ratio (~50%), indicating fresh ventilated surface pollution. Anthropogenic pollution plumes are present from the surface to the upper troposphere throughout spring and summer and contain elevated CO (~170 ppbv in spring and ~150 ppbv in summer) and high C$_2$H$_2$/CO ratio (~2.8 pptv/ppbv in spring and ~1.2 pptv/ppbv in summer). Biomass burning plumes are confined in the mid troposphere during spring with a moderate increase in CO (~220 ppbv) and C$_2$H$_2$/CO ratio (~3.2 pptv/ppbv). The majority of biomass burning air masses sampled during summer are fresh fire plumes in the lower troposphere with marked high CO (~425 ppbv) and C$_2$H$_2$/CO ratio. More detailed analysis on how anthropogenic pollution and Siberian (Spring phase) and Canadian (Summer phases) fire emissions impact atmospheric gas and aerosol composition and O$_3$ production can be found in Singh et al. (2010) and Alvarado et al. (2010).

5. Reactive nitrogen in the Arctic troposphere

Abundance of NO$_x$ plays a determinative role in O$_3$ production in the background troposphere (Lin et al., 1988; Sillman et al., 1990; Jaegle et al., 1998; Wennberg et al., 1998). While NO$_x$ is present in the background atmosphere at low levels, it can be recycled between the radical forms and its long-lived reservoir species, i.e., nitric acid (HNO$_3$) and peroxy acetyl nitrate (PAN), which adds complexity to an accurate understanding of the NO$_x$ budget in the atmosphere. We analyze NO$_y$ (NO$_x$+PAN+ HNO$_3$+nitrates) and its partitioning during ARCTAS to investigate the budget and source attribution of NO$_x$ in the Arctic and sub-Arctic troposphere. It is difficult to quantify the actual contribution of a certain source to reactive nitrogen species (same for O$_3$ in section 6) just based on observations. Therefore we examine the concentration of nitrogen species in individual air masses relative to those in the background. The level of elevated concentration (shown in below as Δ values relative to the background concentrations) in an individual air mass indicates its potential as a source of nitrogen species.

Reactive nitrogen in the background troposphere remains relatively constant from spring to summer (~ 300-400 pptv) (Table 3 and Figures 7 and 8). Nitrogen oxides (~ 25 pptv) on average account for 5-10% of NO$_y$. PAN is the largest reservoir species (~200 pptv), accounting for ~50% of NO$_y$ in spring and ~70% in summer. The level of HNO$_3$ is significantly lower than that of PAN, ~30 pptv in spring and ~70 pptv in summer. A small fraction of NO$_y$ (~6%) is present as alkyl nitrates during summer.

The main sources of NO$_x$ in the high latitudes troposphere are STE, anthropogenic and biomass burning emissions (Figure 7 and Table 3a). Combustion plumes are the major contributors of NO$_x$ in the middle troposphere mainly in the form of PAN and NO$_x$ but little HNO$_3$. STE events are the most significant source of NO$_x$ above 6 km. Air masses associated with STE contain elevated levels of NO$_x$ and HNO$_3$. Compared to air in the lowermost stratosphere, they contain much less NO$_x$ (40% of that in the lowermost stratosphere) and different NO$_x$ partitioning (less HNO$_3$ and more PAN). We calculate the extent of mixing between the air of stratospheric origin with the background based on the mean CO and reactive nitrogen mixing ratios in the three air masses (stratospheric air, air in the tropospheric background, and STE air) (Table 3a). We find that the change in NO$_x$ and its partitioning from stratospheric air to STE air is mainly the result of mixing.
with the background and with negligible net photochemical conversion between NO\textsubscript{x} and its reservoirs.

All sources, including anthropogenic and biomass burning emissions, convection, and STE contribute to NO\textsubscript{y} in the Arctic/sub-Arctic troposphere during summer (Figure 8 and Table 3b). The NO\textsubscript{y} vs. CO relationship is more dispersed during summer, compared to a clear and compact correlation in individual air masses in spring, implying more mixing among air masses of different origin. Biomass burning air mass contains high concentrations of NO\textsubscript{x}, PAN, and alkyl nitrates (ΔNO\textsubscript{x} ~ 600 pptv, ΔPAN ~ 750 pptv, ΔANs ~ 200 pptv) and is the dominant contributor to NO\textsubscript{y} (ΔNO\textsubscript{y} ~ 1700 pptv) in the mid and lower troposphere. Anthropogenic emissions also contribute but their impacts are much less pronounced (ΔNO\textsubscript{x} ~ 65 pptv, ΔPAN ~ 150 pptv, and no elevated ANs and HNO\textsubscript{3}). In the upper troposphere (> 6 km), convection, STE, and biomass burning all contribute significantly to NO\textsubscript{y}. Convection is the dominant source of NO\textsubscript{x} (ΔNO\textsubscript{x} ~ 600 pptv) while upper tropospheric biomass burning plumes is the dominant contributor to PAN. Air masses associated with STE contains high NO\textsubscript{x} comparable to that in convective air mass. The STE air mass displays high NO\textsubscript{x} (ΔNO\textsubscript{x} ~ 100 pptv) and HNO\textsubscript{3} (ΔHNO\textsubscript{3} ~ 400 pptv) as stratospheric air is commonly enriched with NO\textsubscript{x} and HNO\textsubscript{3}.

The STE air is also significantly elevated in PAN (50% more than the background), with mean concentration (~ 320 pptv) almost comparable to that in anthropogenic plumes (~ 355 pptv). The main sources of PAN in the atmosphere are biomass burning and anthropogenic emissions. Oxidation of non-methane hydrocarbons (NMHC) within combustion plumes can rapidly convert NO\textsubscript{x} to form PAN (e.g. Aikin et al., 1983; Singh et al., 1992; Alvarado et al., 2010). Our definition of STE air masses (CO < 160 ppbv for spring and CO < 120 ppbv for summer) excludes the possibility of mixing with fresh combustion plumes which could have contributed to elevated PAN. Further calculation based on mean concentrations of CO and nitrogen species (Table 3b) suggests that mixing with tropospheric background air can increase PAN to ~ 200 pptv in the STE air mass (from 70 pptv in lowermost stratospheric air). The remaining ~ 120 pptv increase in PAN can only be explained by active photochemical production. As air from the stratosphere, which contains high NO\textsubscript{x} and HNO\textsubscript{3}, mixes with the tropospheric background, it provides a direct source of NO\textsubscript{x} as well as an indirect source through releasing NO\textsubscript{x} via HNO\textsubscript{3} destruction. The resulted NO\textsubscript{x} can react with acetyl radicals from the breakdown of acetaldehyde to form PAN. While many NMHC have lifetimes too short to exert a significant impact on PAN production in the background troposphere, ethane (C\textsubscript{2}H\textsubscript{6}), which has a mean atmospheric lifetime of ~ 2 months and up to 10 months in winter (Rudolph et al., 1995; Xiao et al., 2008), is the most likely source of acetaldehyde and has been demonstrated to contribute to PAN formation in the UT/LS (Aikin et al., 1983). Our earlier modeling study, Liang et al. (2009), conducted a detailed budget analysis of NO\textsubscript{x} in the Arctic using the GMI CTM which contains a fully-coupled tropospheric and stratospheric chemistry scheme. The calculated result suggests that significant conversion of nitrogen from HNO\textsubscript{3} to NO\textsubscript{x} and then to PAN within STE air masses in the upper Arctic troposphere during summer. The ARCTAS measurements are in accordance with our theoretical modeling analysis and present the first observation evidence of mixing of stratospheric air with free tropospheric background air as a significant source of PAN in the upper troposphere. This chemical mechanism may likely explain the current difficulty in several tropospheric chemistry transport models (CTMs), in reproducing the observed PAN during ARCTAS (Singh et al., 2010; Alvarado et al., 2010). Unlike GMI, these tropospheric CTMs do not have a well specified stratospheric input of NO\textsubscript{y}, therefore an inadequate representation of PAN production in the Arctic upper troposphere.
6. Ozone and ozone production in the Arctic troposphere

The photochemical balance between O\textsubscript{3} production and loss is an intricate play between NO\textsubscript{x}, HO\textsubscript{x}, and O\textsubscript{3} (Jaegle et al., 1998; Wennberg et al., 1998). In this section, we examine O\textsubscript{3}, O\textsubscript{3} production rate and its dependence on NO\textsubscript{x} and HO\textsubscript{x} to understand the sources of O\textsubscript{3} in the Arctic and sub-Arctic troposphere.

Ozone is produced in the troposphere mainly through the following chemical reactions,

\begin{align*}
\text{OH} + \text{CO} & \rightarrow \text{HO}_2 + \text{CO}_2 \\
\text{HO}_2 + \text{NO} & \rightarrow \text{OH} + \text{NO}_2 \\
\text{NO}_2 + \text{hv} & \rightarrow \text{NO} + \text{O} \\
\text{O} + \text{O}_2 & \rightarrow \text{O}_3
\end{align*}

with reaction (2) being the rate-limiting step. Ozone can also be produced from reaction of peroxy radicals (RO\textsubscript{2}) with NO:

\begin{align*}
\text{RO}_2 + \text{NO} & \rightarrow \text{CH}_2\text{O} + \text{HO}_2 + \text{NO}_2
\end{align*}

Ozone is destroyed in the troposphere through photolysis and reaction with HO\textsubscript{x} (OH + HO\textsubscript{2}):

\begin{align*}
\text{O}_3 + \text{hv} & \rightarrow \text{O}(^1\text{D}) + \text{O}_2 \\
\text{O}(^1\text{D}) + \text{H}_2\text{O} & \rightarrow 2\text{OH} \\
\text{HO}_2 + \text{O}_3 & \rightarrow \text{OH} + 2\text{O}_2 \\
\text{OH} + \text{O}_3 & \rightarrow \text{HO}_2 + \text{O}_2
\end{align*}

We use the O\textsubscript{3} product and loss rates calculated by the NASA Langley box model (Olson et al., 2004) constrained by chemical and physical parameters measured by the DC-8 aircraft. For this study, we use mostly the instantaneous product and loss rates. Note catalytic destruction of O\textsubscript{3} by bromine radicals is also included in the Langley box model to account for the O\textsubscript{3} depletion events sampled during ARCTAS. For simplicity and clarity, we exclude data that contain elevated bromine (BrO > 1.5 pptv). The calculated net O\textsubscript{3} production (formation-destruction) rates, NP(O\textsubscript{3}), can be approximated as:

\[ NP(O_3) = P(O_3) - L(O_3) = K_2[HO_2][NO] + K_5[RO_2][NO] - K_6[H_2O][O(^1D)] - K_7[HO_2][O_3] - K_8[OH][O_3] \]

Figure 9 shows the dependence of the calculated instantaneous NP(O\textsubscript{3}) on levels of NO\textsubscript{x} during ARCTAS for high and low HO\textsubscript{x} conditions and vice versa. While NO\textsubscript{x} concentration remains relatively unchanged from spring to summer, O\textsubscript{3} production rate during summer is ~10 times higher than that calculated for spring, due to active photochemistry with increasing insolation. The level of NO\textsubscript{x} plays a determinative role in the photochemical production of O\textsubscript{3}. The NP(O\textsubscript{3}) increases rapidly with increasing levels of NO\textsubscript{x}, suggesting that the Arctic troposphere is in the NO\textsubscript{x}-limited regime. The rate NP(O\textsubscript{3}) increases with increasing NO\textsubscript{x} is dependent on the abundance of HO\textsubscript{x} radicals. When HO\textsubscript{x} is high (> 4 pptv in spring and > 10 pptv in summer which occur mostly in combustion plumes), the NP(O\textsubscript{3}) increases drastically as NO\textsubscript{x} increases. At low NO\textsubscript{x} concentrations (background and air of stratospheric origin), the NP(O\textsubscript{3}) displays a weak increase with increasing NO\textsubscript{x} as both production (reaction 2) and loss (reactions 7 and 8) are slow. The dependence of NP(O\textsubscript{3}) on HO\textsubscript{x} is rather complex, impacted by levels of NO\textsubscript{x}. On the one hand, HO\textsubscript{x} can enhance O\textsubscript{3} production through reaction (2). On the other hand, it provides a reaction partner for O\textsubscript{3} destruction in reactions (7) and (8). At high NO\textsubscript{x} levels (e.g. fresh combustion plumes, STE events, and convection), the NP(O\textsubscript{3}) show a positive dependence on HO\textsubscript{x} concentrations and increases as HO\textsubscript{x} increases. When NO\textsubscript{x} is low (< 40 pptv, i.e. background and air of stratospheric origin), the
NP(O₃) is either insensitive to HOₓ (spring) or decreases with increasing HOₓ and becomes negative when HOₓ exceeds 20 pptv (summer).

The mean background O₃ in the Arctic and sub-Arctic troposphere remain relatively constant from spring to summer, increasing from 30-40 ppbv at the surface to 60-70 ppbv in the middle and upper troposphere (Figure 10be and Table 3). The middle troposphere (3-8 km) shows net O₃ destruction while the lower (< 3 km) and upper troposphere (> 8 km) has NP(O₃) greater than zero (net O₃ formation), regulated by the mean NOₓ concentration. NOₓ ~ 20 pptv is a critical level (Klonecki and Levy, 1997) in the Arctic troposphere that separates the middle troposphere (NOₓ < 20 pptv, net O₃ destruction regime, Figure 10cf) from the lower and upper troposphere where NOₓ exceeds 20 pptv, hence, net O₃ production (Figure 10cf).

STE events are the most significant source of O₃ in the Arctic during spring and summer, particularly in the upper troposphere (Figure 10). Air mass associated with recent STE intrusions has mean O₃ mixing ratio of ~150 ppbv (vs. ~70 ppbv in background air between 6-12 km). The STE air mass also shows net O₃ formation with instantaneous NP(O₃) as high as ~ 2 ppbv/day in spring and ~ 5 ppbv/day in summer. The change from near zero NP(O₃) in the lowermost stratospheric air to positive values is mainly the result of increasing HOₓ. Air of stratospheric origin contains high NOₓ and its O₃ production rate is highly dependent on the level of HOₓ, as discussed above. As stratospheric air entrains into the troposphere during STE, it mixes with the surrounding background air that has higher water vapor, therefore increases the production of HOₓ and NOₓ concentration. This results in an increase in NP(O₃) from near zero to net O₃ formation.

Convection/lightning is an important source of O₃ during ARCTAS-B. The summertime convective/lightning air mass is elevated in O₃ (ΔO₃ ~ 10 ppbv, Table 3b) and displays high net O₃ production. The springtime biomass burning air mass shows active O₃ production (mean instantaneous NP(O₃) ~ 2 ppbv/day and ΔO₃/ΔCO = 0.22) and an average of 16 ppbv increase in O₃. In contrast, the biomass burning air masses sampled in summer, although showing very high positive NP(O₃) values, display no elevated O₃. Alvarado et al. (2010) conducted a detailed analysis of NOₓ and PAN photochemistry in boreal fire plumes during ARCTAS-B and their impact on O₃ and found little evidence of O₃ formation in the smoke plumes in either the aircraft, satellite, or model results, in accordance with our findings. Paris et al. (2010) also found negative O₃/CO ratio (~0.04 ppbv/ppbv), indicating photochemical destruction of O₃ in the summertime Siberian fire plumes observed during the YAK-AEROSIB/POLARCAT experiment. The seasonal difference in O₃ formation within the biomass burning plumes is likely due to differences in the O₃ production efficiency, defined as the number of O₃ molecules produced per molecule of NOₓ consumed (Jacob 1999). While the NP(O₃) in the summer fire plumes are high, this high production is not sustainable as O₃ production efficiency is low and NOₓ are rapidly converted to PAN in ~2 hours (Alvarado et al., 2010). The anthropogenic air mass in general contains significantly less NOₓ than the other two tropospheric air masses (biomass burning, convection) (Figures 7 and 8) and therefore weaker O₃ production (Figure 10). Despite the positive NP(O₃) rates, the anthropogenic air mass sampled during both ARCTAS-A and ARCTAS-B show no elevated O₃, compared to the background, throughout most of the troposphere.

As we have discussed in section 2.1, measurements obtained during ARCTAS-B are concentrated in the sub-Arctic between 50°N-70°N. The derived conclusions may not represent the true Arctic troposphere as more convection occurs in the continental sub-Arctic and it is closer to pollution sources. We narrow our investigation to focus only on the measurements obtained north of 70°N during ARCTAS-B (Figure 11). While there is significant fraction of convection/lightning air masses identified during ARCTAS-B, none is sampled in the deep Arctic. Air mass associated
with STE events is the only notable contributor to NOx and O3 north of 70°N. In addition, the STE air mass is the only air mass that displays net O3 formation above 2 km. The mean 24-hour averaged NP(O3) (calculated by the Langley box model) in the fresh STE air mass sampled during ARCTAS-B is ~0.9 ppbv/day. These findings confirm our previous proposition that STE, in addition to its direct contribution to O3, is the driving mechanism of net O3 formation in the Arctic upper troposphere as calculated in the GMI Combo CTM (0-10 ppbv/month in July) (Liang et al., 2009).

7. Conclusions

The NASA ARCTAS mission presents a unique opportunity and an extensive suite of measurements to examine O3 photochemistry in the Arctic troposphere. A close look at the observations of CO and the C2H2/CO ratio suggests that the DC-8 aircraft measurements obtained during spring (ARCTAS-A) are representative of the mean Arctic troposphere. Measurements obtained during the summer deployment (ARCTAS-B) are highly biased towards pollution plumes, a fact to consider in understanding the mean chemical composition of the summertime Arctic troposphere and the impact of pollution plumes.

We conducted a detailed analysis using aircraft observations obtained during ARCTAS to examine O3 and NOx in the Arctic and sub-Arctic region and their source attribution. Using a number of marker tracers, we were able to identify various air masses from the background, including anthropogenic pollution, biomass burning emissions, air masses associated fresh stratosphere-troposphere exchange, and convection and/or lightning influences.

The background Arctic troposphere has mean O3 of ~60 ppbv and NOx of ~25 pptv throughout spring and summer. Mean CO mixing ratio decreases from ~145 ppbv during spring to ~100 ppbv in summer. The Arctic troposphere is in the NOx-limited regime with much of the free troposphere shows net O3 destruction due to its low NOx concentration. Extensive aircraft sampling of the Arctic troposphere were available from the earlier Tropospheric O3 Production about the Spring Equinox (TOPSE) campaign in spring 2002 (Atlas et al., 2003) and the Arctic Boundary Layer Expedition (ABLE 3A) during summer 1988 (Harriss et al., 1992). Measurements from these previous missions show a springtime mean CO ~154 ppbv, O3 ~67 ppbv, and NOx ~17 pptv (TOPSE) (Stroud et al., 2003) and a summertime mean CO ~100 ppbv, O3 ~70 ppbv, and NOx ~10-50 pptv (ABLE 3A) (Jacob et al., 1992) at 3-6 km in the Arctic mid-troposphere. Consider the likely variations associated with differences in air mass sampling and interannual variability, the ARCTAS measurements indicate that these important tropospheric trace gases, CO, NOx, and O3, have remain relatively unchanged in the Arctic mid-troposphere in the past two decades, despite the significant changes in processes that could have had a notable impact on the Arctic atmospheric composition, e.g. emissions regulation in European and N. American, rapid industrialization of East Asia, destruction of the stratospheric O3 layer.

Air masses associated with recent stratosphere-troposphere exchange are present at >5 km during spring and summer. These air masses with mean O3 concentration of 140-160 ppbv are the most important direct sources of O3 in the Arctic (>70°N) troposphere. Air of stratospheric origin is also significantly elevated in NOx (mean ~75 pptv in spring and 110 pptv in summer) and HNO3 (mean ~290 pptv in spring and 500 pptv in summer) which will further release NOx through photochemical destruction. Driven by the high levels of NOx, these air masses display active net O3 formation with instantaneous production rates as high as ~2 ppbv/day in spring and ~5 ppbv/day in summer and is the main driver of net O3 production in the Arctic free troposphere. The ARCTAS measurements also present observational evidence suggesting significant conversion of nitrogen
from HNO$_3$ to NO$_x$ and then to PAN within STE air masses during summer (a net formation of ~120 pptv PAN), in accordance with our previous modeling analysis (Liang et al., 2009). This implies that the impact of NO$_y$-enriched stratospheric air on tropospheric NO$_x$, and therefore O$_3$ production, can be extended much further as the resulted PAN is transported to the lower altitudes and releases NO$_x$ downwind through thermal decomposition (e.g. Moxim et al., 1996, Honrath et al., 1996). Although the ARCTAS measurements present clear evidence of stratosphere-troposphere exchange as a significant source of reactive nitrogen in the Arctic troposphere, a quantitative estimate of the impact of the influx of NO$_y$ from the stratosphere on the troposphere NO$_x$, PAN, and subsequently O$_3$ production is yet to be determined through more comprehensive modeling studies.

Although anthropogenic and biomass burning pollution plumes show highly elevated hydrocarbons and NO$_y$ (mostly in the form of NO$_x$ and PAN), there is little evidence that these pollution plumes contribute significantly to O$_3$ in the Arctic troposphere, except the aged Siberia biomass burning plumes during Spring. However, it is important to point out that anthropogenic and biomass burning emissions can still exert an impact on O$_3$ in the Arctic through increasing the background O$_3$ in the mid-latitudes which then enters the polar troposphere through long-range transport, as demonstrated by Shindell et al. (2008). Convection and/or lightning influences are of negligible importance as a source of O$_3$ in the Arctic but can have significant impacts in the upper troposphere in the continental sub-Arctic during summer.

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References.


Table 1. Summary of ARCTAS observations used in this study.

<table>
<thead>
<tr>
<th>Species</th>
<th>Instrument &amp; Methods</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>CO, NO, NO₂, NO₃*</td>
<td>Tunable Diode Laser Absorption Spectroscopy (TDLAS)</td>
<td>Diskin et al. (2002)</td>
</tr>
<tr>
<td>PAN</td>
<td>Chemiluminescence</td>
<td>Weinheimer et al. (1994)</td>
</tr>
<tr>
<td>Alkyl nitrates</td>
<td>Chemical Ionization Mass Spectrometry (CIMS)</td>
<td>Slusher et al. (2004)</td>
</tr>
<tr>
<td>OH, HO₂*</td>
<td>Thermal-Dissociation Laser Induced Fluorescence (TD-LIF)</td>
<td>Cleary et al. (2002)</td>
</tr>
<tr>
<td>CH₃CN*</td>
<td>Laser Induced Fluorescence (LIF)</td>
<td>Brune et al. (1999)</td>
</tr>
<tr>
<td></td>
<td>Whole Air Sampler – Gas Chromatography (WAS-GC)</td>
<td>Blake et al. (2003)</td>
</tr>
</tbody>
</table>

*Multiple sets of measurements were available for several species used in this study, i.e. NO₂, OH, HO₂, HNO₃, CH₃CN. The different measurements broadly agree with each other and the choice of measurements does not affect the conclusion of this study.

Table 2. Air mass characterization criteria.

<table>
<thead>
<tr>
<th>Air mass type</th>
<th>ARCTAS-A</th>
<th>ARCTAS-B</th>
</tr>
</thead>
<tbody>
<tr>
<td>Stratospheric air</td>
<td>O₃ &gt; 100 ppbv; CFC-113 &lt; 78¹ pptv; CO &lt; 80⁵ ppbv</td>
<td>O₃ &gt; 100 ppbv; CFC-113 &lt; 78⁴ pptv; CO &lt; 50⁵ ppbv</td>
</tr>
<tr>
<td>Stratosphere-troposphere exchange</td>
<td>O₃ &gt; 100 ppbv; CFC-113 &lt; 78⁴ pptv; 80⁴ ppbv ≤ CO &lt; 160 ppbv</td>
<td>O₃ &gt; 100 ppbv; CFC-113 &lt; 78⁴ pptv; 50⁵ ppbv ≤ CO &lt; 120 ppbv</td>
</tr>
<tr>
<td>Biomass burning</td>
<td>CO &gt; 160⁵ ppbv; CH₃CN &gt; 145⁴ pptv</td>
<td>CO &gt; 120⁵ ppbv; CH₃CN &gt; 320⁶ pptv</td>
</tr>
<tr>
<td>Anthropogenic</td>
<td>CO &gt; 160⁵ ppbv; CH₃CN ≤ 145⁴ pptv</td>
<td>CO &gt; 120⁵ ppbv; CH₃CN ≤ 320⁶ pptv</td>
</tr>
<tr>
<td>Convection/Lightning</td>
<td>NOₓ &gt; 100 pptv; NO₂/HNO₃ &gt; 1.2 pptv/pptv</td>
<td>NOₓ &gt; 200 pptv; NO₂/HNO₃ &gt; 1.2 pptv/pptv</td>
</tr>
</tbody>
</table>

¹ The 78 pptv threshold is the 25 percentile value for CFC-113.
² The CO ~ 80 ppbv threshold level between stratospheric air and air associated with stratosphere-troposphere exchange are determined based on scattering plots of CFC-113, CH₃CN, SO₂ vs. CO during ARCTAS-A. The CO ~ 50 ppbv threshold for ARCTAS-B is determined based on the scattering plots of CH₄, CO₂, NO₂ vs. CO.
³ The CO ~ 160 ppbv threshold level during ARCTAS-A for biomass burning and anthropogenic pollution is determined by the highest quartile of CO. The CO ~ 120 ppbv threshold during ARCTAS-B is chosen based on the PDF of CO (section 3).
⁴ The CH₃CN ~ 145 pptv for ARCTAS-A and ~320 pptv for ARCTAS-B thresholds are chosen for the optimal segregation between the biomass burning and anthropogenic pollutants based on the CO₂/CO, CH₄/CO, and C₂H₆/CO ratio (supplementary Figures S1 and S2).
**Table 3a.** Mean observed chemical composition of air masses sampled during ARCTAS-A.

<table>
<thead>
<tr>
<th></th>
<th>Background</th>
<th>Anthropogenic Pollution</th>
<th>Biomass Burning</th>
<th>Stratosphere</th>
<th>STE</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>2337 min (58%)</td>
<td>699 min (17%)</td>
<td>168 min (4%)</td>
<td>357 min (9%)</td>
<td>163 min (4%)</td>
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<tr>
<td>0-12 km</td>
<td>0-10 km&lt;sup&gt;b&lt;/sup&gt;</td>
<td>3-9 km&lt;sup&gt;b&lt;/sup&gt;</td>
<td>6-12 km&lt;sup&gt;b&lt;/sup&gt;</td>
<td>5-12 km&lt;sup&gt;b&lt;/sup&gt;</td>
<td></td>
</tr>
<tr>
<td>CO (ppbv)</td>
<td>144±14</td>
<td>156±5</td>
<td>148±9</td>
<td>135±15</td>
<td>172±14</td>
</tr>
<tr>
<td>O&lt;sub&gt;3&lt;/sub&gt; (ppbv)</td>
<td>62±15</td>
<td>48±7</td>
<td>62±9</td>
<td>70±15</td>
<td>57±13</td>
</tr>
<tr>
<td>HO&lt;sub&gt;x&lt;/sub&gt; (pptv)</td>
<td>3.5±1.9</td>
<td>3.4±2.0</td>
<td>3.6±2.1</td>
<td>3.6±1.8</td>
<td>3.2±1.5</td>
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<td>NO&lt;sub&gt;x&lt;/sub&gt; (pptv)</td>
<td>25±65</td>
<td>30±85</td>
<td>20±10</td>
<td>30±20</td>
<td>65±630</td>
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<tr>
<td>PAN (pptv)</td>
<td>205±80</td>
<td>220±60</td>
<td>225±85</td>
<td>180±80</td>
<td>345±145</td>
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<tr>
<td>HNO&lt;sub&gt;3&lt;/sub&gt; (pptv)</td>
<td>30±75</td>
<td>30±35</td>
<td>25±20</td>
<td>35±105</td>
<td>25±30</td>
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<tr>
<td>ANs (pptv)</td>
<td>NA</td>
<td>NA</td>
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<tr>
<td>NO&lt;sub&gt;y&lt;/sub&gt; (pptv)</td>
<td>410±165</td>
<td>420±135</td>
<td>425±160</td>
<td>390±165</td>
<td>650±660</td>
</tr>
</tbody>
</table>
| a For each type of air mass we include the observed mean ± one standard deviation. Chemical species that are significantly enhanced (> mean + one standard deviation) with respect to background at the corresponding altitude are highlighted in bold.  
| b The altitude span of individual air masses.

**Table 3b.** Same as Table 2a but for ARCTAS-B.

<table>
<thead>
<tr>
<th></th>
<th>Background</th>
<th>Anthropogenic Pollution</th>
<th>Biomass Burning</th>
<th>Stratosphere</th>
<th>STE</th>
<th>Convection/Lightning</th>
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<td></td>
<td>1404 min (43%)</td>
<td>1207 min (39%)</td>
<td>325 min (10%)</td>
<td>32 min (1%)</td>
<td>142 min (4%)</td>
<td>61 min (2%)</td>
</tr>
<tr>
<td>0-12 km</td>
<td>0-10 km</td>
<td>3-9 km</td>
<td>6-12 km</td>
<td>0-12 km</td>
<td>10-12 km</td>
<td>6-12 km</td>
</tr>
<tr>
<td>CO (ppbv)</td>
<td>103±11</td>
<td>103±10</td>
<td>104±10</td>
<td>102±12</td>
<td>153±39</td>
<td>426±280</td>
</tr>
<tr>
<td>O&lt;sub&gt;3&lt;/sub&gt; (ppbv)</td>
<td>57±20</td>
<td>34±6</td>
<td>60±15</td>
<td>69±20</td>
<td>58±19</td>
<td>48±17</td>
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<tr>
<td>HO&lt;sub&gt;x&lt;/sub&gt; (pptv)</td>
<td>9.1±5.1</td>
<td>9.1±6.5</td>
<td>10.3±5.0</td>
<td>7.1±2.9</td>
<td>11.8±7.8</td>
<td>16.9±9.8</td>
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<tr>
<td>NO&lt;sub&gt;x&lt;/sub&gt; (pptv)</td>
<td>25±30</td>
<td>35±45</td>
<td>20±20</td>
<td>30±25</td>
<td>90±350</td>
<td>660±1520</td>
</tr>
<tr>
<td>PAN (pptv)</td>
<td>210±100</td>
<td>205±55</td>
<td>230±80</td>
<td>245±95</td>
<td>355±155</td>
<td>970±675</td>
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<tr>
<td>HNO&lt;sub&gt;3&lt;/sub&gt; (pptv)</td>
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<td>90±105</td>
<td>80±85</td>
<td>40±45</td>
<td>90±100</td>
<td>70±70</td>
</tr>
<tr>
<td>ANs (pptv)</td>
<td>20±50</td>
<td>40±70</td>
<td>15±30</td>
<td>10±40</td>
<td>55±90</td>
<td>205±260</td>
</tr>
<tr>
<td>NO&lt;sub&gt;y&lt;/sub&gt; (pptv)</td>
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<td>310±140</td>
<td>365±145</td>
<td>585±445</td>
<td>2055±2200</td>
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<td>2210±260</td>
<td>955±350</td>
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<tr>
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<td>315±165</td>
<td>245±200</td>
<td>310±140</td>
<td>365±145</td>
<td>585±445</td>
<td>2055±2200</td>
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Page 20
Figure captions.

Figure 1. Flight tracks (black solid lines) of the NASA DC-8 aircraft for (a) ARCTAS-A and (b) ARCTAS-B. For this study, we only use measurements obtained north of 50°N. The color symbols indicate the location of various air masses sampled during ARCTAS. Tracks not marked with color symbols indicate background atmosphere.

Figure 2. Comparison of model CO with observations. Panel (a) shows the vertical profile of observed CO (red, error bars indicate the standard deviation of concentrations) and simulated CO (black line) during ARCTAS-A. Stacked influences from individual sources are also shown (green for NH biomass burning, blue for NH anthropogenic emissions, and gray for all other sources). Panel (b) shows the scatter plot of model CO vs. the observations during ARCTAS-A. The black solid line is the regression slope. Panels (c) and (d) are the same as (a) and (b) but for ARCTAS-B.

Figure 3. The probability distribution function (PDF) of observed CO (red line) and GEOS-5 CO (black line) along DC-8 flight tracks for ARCTAS-A. The mean PDF of model CO for April 2008 between 50°-90°N and 130°-180°W is shown in blue shading. For easy comparison with observations, we also include the corrected model CO distribution by shifting +25 ppbv to the right to account for the model low bias (black line-filled shading).

Figure 4. Same as figure 3 but for ARCTAS-B and the corrected model PDF is shifted +15 ppbv, instead of +25 ppbv, to the right to account for seasonal difference in model bias.

Figure 5. Probability distribution functions for the C2H2/CO ratio for (a) ARCTAS-A and (b) ARCTAS-B. We also plot the C2H2/CO ratio vs. CO (insets) to show the strong correlation between the two (r = 0.81 for ARCTAS-A and r = 0.69 for ARCTAS-B). Measurements associated with ODE events during spring (gray dots) and those associated with very fresh biomass burning plumes during summer (green dots) are excluded from the calculation of correlation coefficients for a better demonstration of the linear dependent relationship between CO and the C2H2/CO ratio in mean atmospheric condition.

Figure 6. Vertical profiles of CO and the C2H2/CO ratio during ARCTAS-A (panels a and b) and ARCTAS-B (panels c and b). Black lines show the mean background CO and C2H2/CO ratio at 1-km altitude bins, with gray shading indicating one standard deviation. We use colored symbols to show the individual air masses: stratosphere (purple), STE (lilac), anthropogenic pollution (blue), biomass burning (green), and convection/lightning (yellow). The solid color lines indicate the vertical mean profiles of individual air masses.

Figure 7. Top panels: Scatter plots of NOx, PAN, HNO3, and NOy vs. CO during ARCTAS-A. Bottom panels: Similar to Figure 6, but the 1-km binned vertical profiles of NOx, PAN, HNO3, and NOy during ARCTAS-A. The background air is shown in black and the individual air masses are shown in color: stratosphere (purple), STE (lilac), anthropogenic pollution (blue) and biomass burning (green).

Figure 8. Same as Figure 7 but for ARCTAS-B. Note part of the x-axis in the top panels for CO between 400-1000 ppbv is condensed in length for better visualization of the air mass characteristics.
Figure 9. Panels (a) and (c): The dependence of the instantaneous NP(O₃) on NOₓ for low (blue symbols) and high (red symbols) HOₓ levels during ARCTAS. Panels (b) and (d): The dependence of the instantaneous NP(O₃) on HOₓ for low (blue symbols) and high (red symbols) NOₓ levels. The instantaneous NP(O₃) are calculated by the NASA Langley box model (Olson et al., 2004) constrained by chemical and physical parameters measured by the DC-8 aircraft. We separate data into low NOₓ (HOₓ) and high NOₓ (HOₓ) population using the mean conditions of the corresponding season, NOₓ~40 pptv and HOₓ~4 pptv in spring and NOₓ~40 pptv and HOₓ~10 pptv in summer. The low NOₓ(HOₓ) regime is highlighted in aqua shading on each panel.

Figure 10. Panel (a): Scatter plot of O₃ vs. CO during ARCTAS-A. Panel (b): Vertical profiles of O₃ during ARCTAS-A. Panel (b): Vertical profiles of instantaneous NP(O₃) during ARCTAS-A. Similar to figure 7, the background air is shown in black and the individual air masses are highlighted in color: stratosphere (purple), STE (lilac), anthropogenic pollution (blue), biomass burning (green), and convection/lightning (yellow). Panels (d-f) are the same as (a-c) but for ARCTAS-B.

Figure 11. Vertical profiles of (a) NOₓ, (b) O₃, and (c) instantaneous NP(O₃) between 70°N-90°N during ARCTAS-B. Similar to figure 10, the background air is shown in black with individual air masses highlighted in color: stratosphere (purple), STE (lilac), anthropogenic pollution (blue), biomass burning (green).
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a. ARCTAS-A (Spring)

b. ARCTAS-B (Summer)
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Figure 10. Panel (a): Scatter plot of $O_3$ vs. CO during ARCTAS-A. Panel (b): Vertical profiles of $O_3$ during ARCTAS-A. Panel (b): Vertical profiles of instantaneous NP($O_3$) during ARCTAS-A. Similar to figure 7, the background air is shown in black and the individual air masses are highlighted in color: stratosphere (purple), STE (lilac), anthropogenic pollution (blue), biomass burning (green), and convection/lightning (yellow). Panels (d-f) are the same as (a-c) but for ARCTAS-B.
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