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**Background ozone
over Canada and the
United States**

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Received: 24 August 2009 – Accepted: 21 September 2009 – Published: 7 October 2009

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Published by Copernicus Publications on behalf of the European Geosciences Union.

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Abstract

Planetary boundary layer (PBL) ozone temporal variations were investigated on diurnal, seasonal and decadal scales in various regions across Canada and the United States for the period 1997–2006. Background ozone is difficult to quantify and define through observations. In light of the importance of its estimates for achievable policy targets, evaluation of health impacts and relationship with climate, background ozone mixing ratios were estimated. Principal Component Analyses (PCA) were performed using 97 non-urban ozone sites for each season to define contiguous regions. Backward air parcel trajectories were used to systematically select the *cleanest* background air cluster associated with the lowest May–September 95th percentile for each site. Decadal ozone trends were estimated by season for each PCA-derived region using a generalized linear mixed model (GLMM).

Background ozone mixing ratios were variable geographically and seasonally. For example, the mixing ratios annually ranged from 21 to 38, and 23 to 38 ppb for the continental Eastern Canada and Eastern US. The Pacific and Atlantic coastal regions typically had relatively low background levels ranging from 14 to 24, and 17 to 36 ppb, respectively. On the decadal scale, the direction and magnitude of trends are different in all seasons across the regions (-1.56 to $+0.93$ ppb/a). Trends increased in the Pacific region for all seasons. Background ozone decadal changes are shown to be masked by the much stronger regional signals in areas that have seen substantial reductions of ozone precursors since the early 2000s.

1 Introduction

1.1 Ozone and air quality

Tropospheric ozone is an important component of photochemical smog which has serious health effects on humans (Burnett et al., 1996). The associated costs of health care

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and damage to vegetation can total up to billions of dollars annually in Canada alone (Canada, 2007). As tropospheric ozone is a secondary pollutant, its production and destruction processes are non-linear (Kleinman, 1994; Klonecki and Levy, 1997) which make the temporal and spatial variations in response to precursor emission changes difficult to understand. Ozone also regulates oxidation through the control of hydroxyl radicals (OH), with OH being the dominant “cleansing” chemical in the atmosphere, annually removing gigatons of reactive trace gases and greenhouse gases (Ehhalt, 1999; Prinn, 2003).

1.2 Ozone and climate

As reported by the Intergovernmental Panel on Climate Change (IPCC, 2001, 2007), tropospheric ozone is the third most important anthropogenic greenhouse gas (GHG), following CO₂ and CH₄. IPCC studies have shown that tropospheric ozone is expected to continue rising (Ehhalt et al., 2001) due to the increase in economic activity of many developing countries as they consume more fossil fuel. In short, as the global temperature continues to rise, more favourable conditions for ozone formation will occur (e.g., increased isoprene availability) (Zeng et al., 2008). Since tropospheric ozone is expected to have a direct positive radiative forcing on climate (Ehhalt et al., 2001; Ramaswamy et al., 2001), this continual positive feedback mechanism is projected to warm the earth’s atmosphere in the future. Modeling studies have shown that there is a strong inter-relationship between tropospheric ozone, GHGs, climate and regional air quality (West et al., 2007; Fiore et al., 2008). Therefore, the quantification of different temporal variations of tropospheric ozone through observations is needed in current atmospheric research.

1.3 Background ozone

Background ozone may be considered as the portion of total surface ozone that results from photochemical reactions of biogenic, geogenic precursors and from transport into

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a given area. The mixing ratio of background ozone varies depending on geographic area, elevation, season, and averaging time (Altshuller and Lefohn, 1996). The term *background* is defined here as the planetary boundary layer (PBL) background (similar to what Fiore et al., 2003 defined) consisting of the combination of naturally and anthropogenically produced ozone from outside of Canada and the US, plus naturally formed ozone within Canada and the US. The term *background* is hereafter to be understood as the Canadian and US background.

1.4 Temporal variations of tropospheric ozone

Ozone mixing ratios observed at remote locations are the result of ozone that is produced and transported over long distances from upwind precursor sources (anthropogenic and natural). Therefore, depending on the upwind locations of precursor sources, tropospheric ozone is expected to be heterogeneously distributed in time and space. Its atmospheric lifetime has been shown to be highly variable, from hours to weeks depending on time of the day, season and location (Schultz et al., 1999; Ehhalt et al., 2001; Fiore et al., 2002). Factors that control the lifetime of ozone are not easily separable (Wild, 2007). The observed long-term ozone trend at a given site, is therefore, expected to be obscured by the mixing of trends (possibly opposing) in the free troposphere (the hemispheric signal) and in the PBL (the regional and/or local signals). The magnitude and the direction of the long-term trends, especially for secondary pollutants such as ozone are difficult to discern and explain most of the time (Weatherhead et al., 1998; Jonson et al., 2006).

1.5 Air quality policy implications of background ozone

To further highlight the importance and quantification of background ozone, the following is a brief review of its implications on air quality policy. The air quality standard set by any jurisdiction must be attainable via domestic anthropogenic emission controls. The component due to emissions within a region has sometimes been referred to as

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controllable ozone or *policy relevant ozone* (Fiore et al., 2002, 2003; Reid et al., 2008), and refers to the amount that is possible to be controlled within one jurisdiction. By definition then, the background of ozone cannot be reduced by precursor emission controls within Canada and the US. The magnitude of the effect of background has been shown in modelling studies to vary in different regions across the US (Fiore et al., 2002, 2003). The estimated background in our study may be by various degrees influenced by regional anthropogenic sources (Altshuller, 1987; Altshuller and Lefohn, 1996). Thus, if the (continental and/or regional) background is indeed rising, the actual “controllable” amount by one local jurisdiction may become smaller in the future.

1.6 Previous research on background ozone

The quantitative values of background ozone in the PBL over the US have been estimated from both observations (Altshuller and Lefohn, 1996) and global chemical transport models (GEOS-Chem) (Fiore et al., 2002, 2003; Wang et al., 2009). Various papers have shown significant increasing *background* ozone trend results in the Northern Hemisphere (Jaffe et al., 2007; Parrish et al., 2009, Chan, 2009) while other papers have reported no significant changes (Oltmans et al., 2006, 2008). In Chan (2009), a multiple-site ensemble time series modelling technique was applied to characterize a decadal change in the ozone mixing ratios. This was done using different averaging metrics for the period 1997 to 2006 for many regions in Canada and the US. The evidence from that particular study showed that ozone trends decreased significantly in southeastern Canada and the eastern US, whereas trends in coastal regions increased. No data screening was done to determine ozone mixing ratios associated solely with the background air.

1.7 Research questions

The foregoing research leads to a number of questions that are addressed in this paper. The questions follow: Does the background mixing ratio vary homogeneously over

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large areas of North America? Given the large intra-annual variations (noise) in ground level mixing ratios relative to the magnitude of the long-term trends (signal of interest), can the background ozone decadal trends still be reliably detected and, if so, what are they? How are the directions and magnitudes of such trends different in the four seasons in different regions of Canada and the US? Are the domestic precursor reduction efforts in Canada and the US important for controlling regional-scale pollution in light of rising background ozone mixing ratios?

1.8 What is new in this study?

As mentioned above, it is difficult to define and quantify background ozone. Nonetheless, there has been a tremendous amount of effort made in the past to identify and separate different spatial (continental, regional, and local) and temporal (multi-year, seasonal, and diurnal) signals superimposed on each other. Backward trajectories have widely been used to classify air parcel transport using various statistical clustering methods. Not limited to tropospheric ozone, a variety of atmospheric constituents have been investigated in the last few decades using trajectories (Dorling, 1992; Moody et al., 1995; Pochanart et al., 2001; Vet et al., 2005; Bottenheim and Chan, 2006; Worthy et al., 2009, and many others). However, Parrish et al. (2009) have argued that continental effects cannot be reliably eliminated by using large scale meteorological data such as air parcel trajectories. Undoubtedly, there is no universal method for all situations. The method introduced here is new in that it selects the *cleanest* or *background* trajectory cluster which is associated with the lowest May–September 95th percentile of ozone (least amount of regional photochemically-formed ozone) for every measurement site. Consistent selection of *background* air for all sites is demonstrated. As opposed to earlier work that provides an annual median background levels (Fiore et al., 2003; Vingarzan, 2004), here the diurnal and seasonal variations (cycles and trends) of the background ozone levels were calculated. The confidence of the decadal trend analysis in this paper is strengthened by employing an ensemble site approach to the time series modelling (Chan, 2009). What is different from Chan (2009) is that

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the regional decadal trends of background ozone are estimated for the four seasons separately by region. The same statistical technique is applied throughout this paper to provide statistical consistency between the trend estimates of the various regions. This study provides a comprehensive analysis of background ozone variations in different chemical regimes over Canada and the US for the first time instead of focusing only on the west coast as in previous studies (Jaffe et al., 2007; Oltmans et al., 2008; Parrish et al., 2009).

2 Data sources

The tropospheric, *non-urban* ozone data used in this study were obtained from the Canadian Air and Precipitation Monitoring Network (CAPMoN), the Canadian National Air Pollution Surveillance Network (NAPS), and the United States Clean Air Status and Trends Network (CASTNET) of the US Environmental Protection Agency and National Park Service (NPS). In all, ninety-seven non-urban sites were used in the two countries, spanning latitudes from approximately 29° N to 55° N, and longitudes from 65° W to 123° W. The altitudes of the site locations ranged from 2 to 3178 metres above sea level. Non-urban sites were used to minimize as much as possible local influences present in the data. Temperature observations, used to remove temperature effects in decadal ozone trends, were obtained from the Canadian Climate Archive for ozone sites located in Canada and from on-site CASTNET temperature observations for sites in the US.

In the CAPMoN network, the sites are located in rural or remote areas and are considered to be regionally representative. In the NAPS network, only the few sites located in rural locations were used, although, in general, they may have been more influenced by pollution from upwind urban areas than the sites in CAPMoN and CASTNET. Similar to CAPMoN, the CASTNET sites are rural in nature. Six-hour averages of hourly ozone values at the measurement sites were used for the investigation of seasonal variations. To avoid the influence of the nocturnal boundary layer and its related effects of local

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emissions, nighttime scavenging and dry deposition, daytime averages (12:00–18:00 local standard time (LST)) were used for studying the decadal trends, i.e., the time when the PBL is fully developed and the air is expected to be well-mixed. Only sites with 75% or more data capture for every season for both ozone and temperature were used.

Three-day air parcel backward trajectories produced by the Canadian Meteorological Centre (CMC) were used to sort the six-hour-average ozone mixing ratios for this analysis. The trajectory calculations were made at that 925 hPa to avoid the influence of surface effects. At this level, the air flow is typically within the PBL (the mixed layer), well below the free troposphere and well above ground level. The CMC trajectory calculations are based on the Canadian Meteorological Centre's Global Environmental Multiscale (GEM) model (Côté et al., 2007). The trajectory calculations are not based on isentropic or isobaric assumptions. Trajectories calculated with the backward mean-trajectory model (BAM) show the 3-D displacement by mean wind vector at six-hour intervals. Trajectories were calculated for arrival times at the measurement sites of 00:00, 06:00, 12:00, and 18:00 UTC every day.

3 Statistical method

3.1 Background ozone estimation

The method developed in this study uses the knowledge of ozone temporal behavior in response to regional photochemistry, combined with clustering of air parcel trajectories, to objectively select the *cleanest* and *most polluted* air trajectory clusters for each site. The *cleanest* clusters are assumed to represent *background* air. The most-polluted clusters have been included here as a basis for comparing and contrasting the results of the *cleanest* clusters. Seasonal background levels and temporal variations were calculated by fitting a one-year harmonic cycle to all six-hour-average data associated with the *cleanest* clusters for seven regions, namely: coastal/continental

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Eastern Canada, continental Eastern US, coastal/continental Western Canada, and coastal/continental Western US regions. Similarly, the diurnal background ozone levels and variations were estimated by fitting a 24-h cycle to all the hourly data associated with the *cleanest* air clusters for different seasons for a given region.

5 3.2 Seasonal principal component analysis

Principal Component Analysis (PCA) (SAS/STAT[®], 1990) was done to identify ozone measurement sites that should be grouped together and thereby form different regions for the regional trend analysis that follows. The objective here was to use PCA to maximize the total variance that could be accounted for by as few physically-meaningful regions as possible (Chan, 2009). PCA is a dimensionality reduction technique that makes no attempt to form regions with equal numbers of sites. The regional groupings were formed using the correlation matrix calculated from the six-hour-average ozone mixing ratios from the 97 non-urban CAPMoN, NAPS, CASTNET and NPS sites for the period 1997–2006 during the months of March-April-May (MAM), June-July-August (JJA), September-October-November (SON) and December-January-February (DJF). Similar to Eder et al. (1993), varimax orthogonal rotation was used in this study. Seventy-five percent was the minimum total variance that had to be accounted for by the number of the underlying principal components in each season.

3.3 Backward air parcel trajectory clustering

A k-means clustering technique (Dorling et al., 1992) based on Euclidean distance was used to sort the three-day air parcel backward trajectories from 1997 through 2006 into six trajectory clusters for each site. The method of determining the number of clusters (6) was the same as that used in Dorling et al. (1992). A graph was plotted for the total root mean square deviation (TRMSD) of all individual clusters from their cluster mean vector against the number of clusters retained. A jump in the TRMSD plot (not shown) at seven clusters indicated that six was the optimal number of clusters that

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should be used. Six clusters were found to be common to most sites and were therefore used throughout this study. In this context, trajectory clusters were considered to characterize the 10-year air flow climatology affecting the measurement sites.

With every six-hour trajectory at a site now being associated with one of six trajectory clusters, it was possible to bin the six-hour average ozone mixing ratio associated with each trajectory to its appropriate trajectory cluster. Then, the 95th percentile ozone mixing ratio for May to September was calculated for every trajectory cluster. For each site, the *cleanest* background trajectory cluster was chosen as the one associated with the lowest 95th percentile of the six clusters. This cluster was assumed to represent background air flow with the least influence of regional/local-scale photochemically-produced ozone, which generally contributes to peak levels in the summer. Thus, the least regional/local anthropogenic influences from Canadian and US emissions should be expected from these background clusters. For contrast, the opposite was also done to identify the *most polluted* trajectory cluster associated with the highest 95th percentile at each site.

3.4 Seasonal and diurnal variations using LOWESS

LOcally WEighted Scatter plot Smoothing (LOWESS) (Cleveland et al., 1988; SAS/STAT[®], 1990) was used to display the seasonal and diurnal variations at each site in each PCA-derived region using the JJA-month groupings. The smoothing parameter was chosen so that the periodicities of the temporal variations shown were between a month and a year for the seasonal variations, and less than 24 h for the diurnal variations.

3.5 Regional decadal trends for different seasons

The robustness and the statistical significance of the decadal trends at individual sites are lower than desired because the data set comprised only the subset of data corresponding to the background air trajectory cluster. To improve the statistical power

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and discern a decadal ozone trend for each PCA-derived region as a whole, a generalized linear mixed model (GLMM) (SAS/STAT[®], 2006), which serves as a multiple site ensemble technique, was used. The details of the time series model have been previously described in Chan (2009), but here it was run for each season separately.

In the time series model, the effects of inter- and intra-annual variations due to warmer versus colder weather were accounted for by using the daily maximum 1-h temperature as the covariate. The model also contained a one-day autoregressive term. Sine and cosine terms with three- to five-year periodicities were used to model the decadal trend component instead of a polynomial, which is often used. This was done to avoid collinearity with the linear slope term with respect to time. Neither one-year nor six-month harmonic terms were included because the regional trend analyses were done for different seasons separately.

4 Results and discussion

4.1 Background ozone estimation

The quantitative estimates of seasonal background ozone are shown in Table 1a. These represent the final calculations and are given here before showing the intermediate steps that produced them. Using the *cleanest* data sets to represent *background* ozone, the ranges (minimum and maximum) of the mean seasonal cycles shown in Table 1a were calculated using a least-squared fit with a one-year cycle to all the six-hour-average ozone mixing ratios associated with the *cleanest* background trajectory clusters in a given region. This calculation was done for sites in coastal and continental areas of Eastern Canada, Eastern US, Western Canada and Western US separately. Background ozone levels varied seasonally in all regions. For example, the mixing ratios ranged from 31 to 38 in spring (28 to 38 in winter), and 33 to 38 (24 to 33) ppb for continental Eastern Canada and Eastern US, and, 22 to 24 (15 to 23) and 39 to 44 (35 to 39) ppb for coastal Western Canada and coastal Western US, respectively.

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These disparities in ranges are due to high elevations in the west compared to the east, and the close proximity to densely located ozone precursor emission sources for a large number of sites in the east. The values of the ranges for Canada are considerably lower than those for the US during the photochemically active seasons of spring (MAM), summer (JJA) and fall (SON). In coastal locations, the ranges are generally lower than those in continental locations regardless of the season. Note that PC1, PC5, PC6, PC8, PC10 and PC11 (based on PCA-derived regions for JJA) show similar seasonal variations and ranges with no apparent summer maxima which is typically associated with regional photochemically-produced ozone.

Similarly, as shown in Table 1b, the ranges of the mean diurnal cycles were calculated by fitting a 24-h cycle to all the hourly ozone mixing ratios associated with the *cleanest* background clusters in a given region. This calculation was done for the four seasons separately. For instance, the results of the diurnal cycles of the ozone mixing ratios associated with the *cleanest* background clusters for coastal Eastern Canada estimated for the MAM, JJA, SON and DJF months ranged from 30 to 39, 13 to 30, 16 to 26 and 29 to 33 ppb, respectively. Serving as a diagnostic analysis tool, the amplitude of the diurnal cycle indicates the degree of local influence, with the wider the range, the greater the local influence (e.g., local precursor emissions). Generally, the ranges of the diurnal cycles are narrower for Canada than for the US during the photochemically active seasons, except for continental Western US where the ranges were the narrowest.

4.2 Seasonal principal component analysis

The varimax orthogonal rotation identified 13, 14, 11, and 8 PCA-derived regions for the MAM, JJA, SON, and DJF months, respectively. The PCA-derived regions (or principal components) were ordered by the percentage of the total variance explained from the largest to the smallest. Sites that were grouped together had the largest loadings associated with that particular principal component.

Figure 1 shows, for the four seasons, the different PCA-derived regions (clusters) of

measurement sites. The large number of regions suggests that, as one would expect, major between-region differences exist in emission source strengths and locations, air mass transport climatologies and atmospheric chemistry regimes. In general, from season to season the same regions exist with the exception of winter, in which there were fewer regions – indicating more spatial homogeneity than the other seasons. The presence of the same regions from season to season suggests that all within-region sites share common air mass transport climatologies, precursor emissions and chemical reaction mechanisms. Figures 2, 3 and 4 support this.

Figure 2 shows, for each season, the 10-year-average backward trajectory (three day) at each site. It can be seen that the average air flow trajectories for all sites in a given region have similar average flow directions. This implies that the precursor emission sources in the upwind direction are sufficiently similar for all sites in a given region.

This is further demonstrated by a Canadian chemical transport model, AURAMS (See Appendix), which was used to produce the seasonal domain-average mixing ratio fields from the anthropogenic and natural emission sources of NO_x and isoprene (Moran, 2009). The fields (Figs. 3 and 4) were produced from a 2002 AURAMS annual simulation base case run. NO_x ambient mixing ratios do not vary substantially from season to season, but generally are higher in winter (DJF). Thus, only the NO_x mixing ratio spatial distribution in JJA is shown. In contrast, the predicted isoprene mixing ratio fields show four distinctively different spatial distributions. This is because the isoprene ambient mixing ratios are closely related to isoprene emissions from biogenic sources, which have strong seasonal variations caused by varying solar intensities throughout the year.

During the spring (MAM in Fig. 2), strong northwesterly flows predominate in the east of the continent, whereas strong westerly flows from the Pacific Ocean predominate in the west. Since the transport pathways and origins are very similar at all sites in the east during the spring (Fig. 2), one might expect a priori that eastern sites would be grouped together by the PCA analysis. The fact that different site clusters were found

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suggests that, in general, the spatial distribution of precursor sources and their related emission strengths are more important than the transport patterns alone in terms of affecting ozone variability in this part of the continent. Indeed, the PCA-derived regions are largely similar to the high levels of the predicted NO_x and isoprene ambient mixing ratio fields (Figs. 3 and 4). It appears that for example, the grouping of PC3 (Mississippi, Alabama, Georgia and Carolina US) is the result of high upwind NO_x mixing ratios from eastern US mixing with high regional isoprene from within the southeastern states. On the contrary, the grouping of PC8 (Alberta CA) may be due to regional NO_x sources from within Alberta, Canada combining with high upwind isoprene mixing ratios originating in British Columbia, Canada.

In contrast, during the summer (JJA), the PCA-derived regions correspond roughly to the different mean transport patterns previously shown in Fig. 2. For instance, the short length and curvature of the mean trajectory paths in PC3 and PC4 (Illinois, Indiana and Ohio US) indicate a predominate stagnant air situation in the area. This recurring flow pattern in the east is attributed to clockwise air flow around the back side of stagnant high pressure systems which transport polluted air masses northward (Lyons and Cole, 1976; Wolff et al., 1977; Wolff and Lioy, 1980). In addition, the two upwind high isoprene mixing ratio areas (dark brown, above 4 ppb) in the southeastern US (Louisiana, Arkansas and Missouri) appear to coincide with the mean flow direction for PC3 and PC4. For example, the groupings in the west appear to coincide roughly with the regional NO_x and high isoprene emission source areas in California. In general, the speed of the air flows is slower in the summer in most regions compared to other seasons indicated by the relatively short distance range of the backward trajectories.

During the fall (SON), the air flows are in transition from being predominately slow-moving and regionally/locally representative to becoming rapid and continentally representative. The spatial distribution of the isoprene mixing ratios is generally similar to the one in the spring. For instance, the predominant northwesterly transport pattern of PC1 (southern Quebec CA) suggests that southern Ontario and southern Quebec

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NO_x sources, and northern Ontario and northern Quebec isoprene sources (possibly from Canadian boreal forests) contribute to the ozone variability of this particular PCA-derived region.

During the winter (DJF), the mean air flow directions are relatively homogeneous between and within regions and traverse over longer distances than in other seasons. In other words, the meteorological influence is dominated by the continental wind flow pattern. Therefore, it is not surprising to see that the very narrow range of the diurnal variations (29–33 ppb, Table 1). This is partially the result of the wintertime longer-range and higher altitude transport that brings in clean background air, the low level of photochemical ozone production due to the reduced solar irradiance intensity, and the much reduced regional/local isoprene mixing ratios (Fig. 4). In short, the winter PCA-derived regions do not compare directly with the spatial distributions of NO_x and isoprene mixing ratios but fit well with the mean transport patterns.

4.3 Backward air parcel trajectory clustering

Egbert (44°13'57" N, 79°46'53" W), located in southwestern Ontario, Canada, was selected to illustrate the use of trajectory clustering to classify ozone data. First, six trajectory clusters were established (Fig. 5a) for this and every site. Then, each six-hour average ozone mixing ratio was allocated to its associated backward trajectory and binned into its appropriate trajectory cluster. In Fig. 5a, the cluster number (C1 to C6) is shown on the top left of each cluster panel and the relative transport frequencies, in percentages for different seasons, are shown at the bottom left corner. For example, C1 represents the cluster of southwesterly flow trajectories and contains a total of 2471 (17%) trajectories over the period 1997–2006. Comparing across the six clusters for the same season, the transport frequencies attributed to this cluster are 15%, 17%, 20%, and 16% during spring (MAM), summer (JJA), fall (SON), and winter (DJF), respectively. Figure 5b shows a monthly box-and-whisker plot of the six-hour-average ozone mixing ratios associated with the six clusters. The May–September 95th percentiles for the southwesterly flow (C1) and northerly flow (C6) are shown as the red

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and yellow horizontal bars, respectively. C6 was selected to represent the *cleanest* background air for this site because the associated May–September 95th percentile mixing ratio is the lowest (yellow bar) compared to the other five clusters. The choice of this cluster as representing background air is further validated by this figure as it shows that a summer maximum, which is attributable to regional photochemically-produced ozone, does not exist in C6. Additionally, the 5th percentile (lower whisker) value is the highest of the clusters in winter, suggesting that it is representative of continental background ozone because it has not undergone destruction processes typical of the clusters influenced by western and southern NO_x emission areas.

Monthly 95% multiple Bonferroni test results are shown at the top of Fig. 5b where the Bonferroni test is a conservative test used to control family-wise error with normally distributed data such as ozone. The order of the clusters is from the highest (at the top) to the lowest (at the bottom) monthly mean mixing ratios associated with the clusters. Vertical bars that overlap clusters indicate that there is no evidence of significant statistical differences between those clusters; alternatively, clusters not joined by vertical bars are considered to be statistically significantly different. For example, identified as the *cleanest* background cluster, C6, this northerly flow cluster tends to have the lowest monthly mean ozone mixing ratios during the summer months. However, the Cluster 6 mean is not significantly different from the C4 mean, where C4 is a shorter transport cluster that has more northerly and easterly components than C6. The Bonferroni testing therefore clarifies that the background mixing ratios (significantly lower in summer) are associated with predominantly northwesterly and/or northerly flow. The *most polluted* cluster, C1, is often associated with the highest monthly mean ozone mixing ratios during May through October and the means are always significantly different from the other clusters in the warm months.

Note that the statistics that were used to select the background trajectory clusters were based on May to September ozone data while the trajectory clusters themselves corresponded to all months in the 1997 to 2006 period. Figure 6a and b shows the *cleanest* and *most polluted* air parcel trajectory clusters for the most statistically repre-

sentative site in each region which was chosen as the site with the largest communality value associated with the respective principal component for the JJA months. Note that the larger the communality of a site in the principal component, the better the site is explained by the respective principal component and thus, the more representative it is of the region. In Fig. 6b, the trajectory clusters shown are the ones associated with the highest May–September 95th percentile ozone mixing ratios of the six clusters at each site. These clusters represent the *most polluted* air flows affecting the sites in order to provide a contrast to the *cleanest* background air flows shown in Fig. 6a.

Generally, the *cleanest* or *background* air clusters (Fig. 6a) for non-coastal sites are associated with northerly Arctic flows whereas, for coastal sites, they are associated with oceanic (Pacific or Atlantic) flows. For the most part, the background air trajectory clusters traverse areas with minimal regional anthropogenic precursor sources (see the predicted NO_x mixing ratio spatial patterns in Fig. 3 and the population density map shown in the centre of Fig. 6a). Although less important for the non-urban sites used in this study, it is important to note that the background value for each site may be affected by ozone removal processes such as dry deposition and NO scavenging. The existence of such removal processes were evaluated by selecting the *most polluted* air clusters as discussed later in this section. The *background* air cluster selection is also confirmed by the transport frequency statistics shown at the lower left corner of each trajectory probability density panel. The statistics show that relatively frequent air flows are attributed to the spring (MAM) and winter (DJF) months. These are the months when background air is typically being transported at higher altitude and over longer distance in the northern mid-latitudes (Wang et al., 2003).

Figure 6b shows the *most polluted* clusters for the same 14 selected sites, one in each region. In fact, the areas of highest transport probability densities for these clusters are (yellow-to-red) the same areas in which high NO_x mixing ratios are predicted by AURAMS (Fig. 3). For instance, in the east, the trajectory cluster of PC1 (similar to PC2, 3, 4, 5, 6, 11 and 13) coincides with high NO_x mixing ratios in locations including Southern Ontario/Canada, Illinois, Indiana and Ohio states/US, Boston-Washington

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DC corridor. In the west, the *most polluted* clusters of PC8 and PC12 coincide with high NO_x mixing ratios in Southern Alberta/Canada and the west coast of California/US, respectively. In this *most polluted* set of clusters, the transport distance is shorter and closer to the surface (see Fig. 7a and b for average transport height of the background and most polluted clusters). Focusing on regions least affected by mountainous terrain, the average transport height of the *cleanest* set of clusters is consistently about one km higher than the *most polluted* set of clusters. As well, the transport frequency statistics for most sites show opposite flow characteristics to those of the *background* air clusters, i.e., the *most polluted* set of clusters have relatively frequent air flows during the summer (JJA) and fall (SON) months, when photochemistry is at maximum, compared to other seasons.

4.4 Seasonal variations

One of the questions posed in the Introduction was whether domestic ozone precursor emission reduction efforts might still be important in light of the documented (see Sect. 4.6) increase in background ozone. Evidence is provided in the following sections to address this question.

Many studies in the past have discussed the seasonal variations of tropospheric ozone. Typical of ozone in the Northern Hemisphere is a spring maximum (Simmonds et al., 1997; Monks, 2000), formed partly from enhanced photochemistry in the springtime after a wintertime accumulation of air pollutants (Penkett and Brice, 1986) and partly from a downward flux of stratospheric ozone (Daniesen and Mohnen, 1977; Viezee et al., 1983). A second characteristic is a summertime maximum that occurs in regions strongly affected by the photochemical production of ozone due to precursor emissions (Singh et al., 1978; Logan, 1985).

To investigate whether these characteristics occur at the sites in this study, the seasonal variations of ozone associated with the *cleanest* and the *most polluted* clusters for all sites are shown in Fig. 8a and b. The reason that the JJA set of site groupings was used was because it had the most regions, and thereby revealed the spatial homo-

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geneity (or inhomogeneity) of the seasonality in background ozone. With reference to the *cleanest* air clusters in Fig. 8a, the high springtime ozone peak and the lack of high summertime values in all but regions, PC2, PC3 and PC4 suggest the lack of active local or regional photochemical ozone production (Goldstein et al., 2004), but rather the influence of long-range transport to the site with air descending either from the Pacific, Arctic or Atlantic Oceans, as shown earlier. In contrast, precursor-source-influenced air in Canada and the US appears to be strong in PC2, PC3 and PC4 (eastern, south-eastern and Midwest US) because of the presence of high summertime values. Not surprisingly, this suggests that, even for these non-urban sites, the importance of the background diminishes for sites located very close to high density precursor sources and in areas where the frequency of subsidence inversions is high (Fiore et al., 2002, 2003). In addition, because of the similarity of the within-region seasonal profiles and the narrow range of variabilities over such large spatial scales, the method developed here provides confidence that the selection of the background air is satisfactory with the minimal existence of any regional photochemical signals in most of the regions. This evidence also suggests that the subset of background ozone mixing ratios teased out from the entire data set of non-urban sites is spatially consistent and continental (possibly hemispheric) in nature with the exception of regions PC2, PC3 and PC4. It is interesting to note that the values of the spring maxima for the sites at higher elevation (PC7 and PC9) are very comparable to those closer to sea level. However, the summer minima of the seasonal cycles at the high elevation sites are, in general, not as low, possibly because of fewer removal processes taking place at high elevation.

By way of contrast, the seasonal variations associated with the *most polluted* air trajectory clusters (Fig. 8b) show that most of the measurement sites have the incrementally-enhanced spring maximum and the broad summer maximum, both of which are typically associated with the photochemical oxidation of ozone precursors in areas associated with high precursor emission sources. The relatively wide range of the inter-percentile bars (the monthly 5th to 95th percentiles of all sites within the PCA-derived region) shown in Fig. 8b, compared to Fig. 8a, indicates that more

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regional/local processes have affected the local ozone mixing ratios.

4.5 Diurnal variations

Diurnal cycles, plotted by season and by region, allow one to investigate the relative intensity of local ozone influences including boundary layer dynamics, photochemical production and dry deposition. The inclusion of diurnal variations in the analysis helps to evaluate the degree of local impacts that potentially exist in the extracted background ozone data.

Figure 9a and b shows the average diurnal cycles of ozone associated with the *cleanest* and *most polluted* air clusters by season for each PCA-derived region, respectively. Diurnal variations that peak in the afternoon are influenced by the combined effects of vertical entrainment of air from aloft by the growing convective PBL, the inflow of ozone due to transport from outside the location, and in-situ photochemical production. Nighttime and early morning decreases in mixing ratios are expected to occur more from surface destruction than from chemical scavenging because of the non-urban nature of the sites (i.e., distant from major NO_x sources) (Singh et al., 1978). In this study, additional insights are gained from the large number of non-urban sites affected by minimal-to-high regional NO_x and isoprene emission sources, and low and high elevation areas in Canada and the US.

In general the diurnal cycles associated with the *most polluted* air are about a factor of two higher than those associated with the *cleanest* air throughout the day during the summer (JJA, red curves) and always lower during the winter (DJF, blue curves). The only exception to this is PC13, for which the nocturnal minimum associated with the *most polluted* air cluster is lower than that associated with the *cleanest* air cluster, although the daytime maximum associated with the *most polluted* air cluster is higher than that associated with the *cleanest* air cluster. This suggests that, at the one forest-dominated site that defines this region, strong daytime local photochemistry and nighttime chemical scavenging dominate over ozone inflow. In other words, the diurnal cycles at every other site in the map domain suggest that long-range transport

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dominates over other processes affecting ozone variability at non-urban sites. This provides further confidence that the non-urban site selection in this study is appropriate for estimating background ozone levels.

Because the air parcel transport heights (Fig. 7a and b) are higher for the *cleanest* clusters than for the *most polluted* clusters, the *cleanest* clusters are expected to have more influence of downward entrainment of high elevation ozone. However, the diurnal cycles associated with the *most polluted* air are always of higher amplitude than those associated with the *cleanest* air in the daytime during the summer (JJA). This suggests that additional amounts of inflow ozone are transported to the sites from upwind precursor sources, which dominates over the ozone that is vertically mixed down to the surface during the day and is scavenged and/or surface deposited during the night.

The mixing ratios associated with the diurnal cycle of PC9 for the *cleanest* clusters are the highest of all regions (Fig. 9a). Theoretically, without additional local photochemical production, the maximum diurnal mixing ratios in other regions should not exceed this upper limit of 50–55 ppb. Note that this upper limit is similar to the one for Europe reported by Chevalier et al. (2007) of about 40–60 ppb above the top of the planetary boundary layer (at approximately 3 km). The evolution of the diurnal cycle should, for “pristine” sites at mid-latitudes (completely free of precursor sources), be the direct result of the development of the growing convective boundary layer and the mixing of high ozone upper air downward to the surface (Singh et al., 1978). For the most part, this appears to be true for the ozone data associated with the *cleanest* background air clusters. However, as shown in Fig. 9b, this upper limit remains more or less the same for the *most polluted* air flows in PC9, but the daytime ozone peaks in many regions do exceed this upper limit. This suggests that local photochemically-produced ozone does not exist in the *cleanest* background air clusters, but does exist in the *most polluted* air clusters.

Although orographic effects can lift low altitude regional ozone precursors from the surface to high elevations, most high elevation measurement sites are expected to be exposed to air from the free troposphere more frequently than low elevation air. As

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a result, smaller diurnal variations should occur at the high elevation sites than at sites near or at sea level. This is indeed the case for PC9, the region that contains the highest elevation sites. Here, mixing ratios decrease only minimally at night (Fig. 9a) which, in turn, suggests that depositional and chemical losses are minimal at night.

5 Similarly, the lack of a strong daytime maximum suggests that daytime production of ozone from local precursors is minimal or, in other words, long range transport of non-locally-produced ozone is the dominant source of ozone at these high elevation sites.

4.6 Regional decadal trends for different seasons

The foregoing trajectory clustering technique allowed us to produce estimates of *back-*
10 *ground* ozone in North America. The analysis was extended further to produce estimates of the decadal trends of North American background ozone. To that end, decadal trends of daytime (12:00–18:00 LST) average ozone mixing ratios were modelled using the GLMM technique for the four seasons and for all PCA-derived regions. The results are shown in Table 2, for only the trend estimates that are statistically significant at the $p < 0.05$ level. Figure 10 shows the trend results in map form with all
15 statistically significant trends being shown with a black line at the regional boundary. For comparison, Table 3 provides a tabulated summary of background ozone trends from three recently published papers that have investigated the trends of inflow air impacting the coastal areas of North America (Jaffe et al., 2007; Oltmans et al., 2008; Parrish et al., 2009). This paper uses a multi-site modelling approach to draw regionally
20 representative conclusion compared to single-site trend analysis in previous studies.

It is important to note here that the direction of the decadal trends in Table 2 is more robust than the magnitude of the trends. This is because the estimated magnitude depends on many factors, including: 1) the statistical method chosen, 2) the model formulation and parameterization, 3) the representativeness of the rather small number
25 of data in the *cleanest* trajectory clusters (4 to 25% of the total data set from Fig. 6a), 4) the data period, and 5) the fact that the magnitude of the decadal trend is generally much smaller (less than one ppb per year) than the other shorter time scale signals

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in the data (tens of ppb from day to day). In light of the fact that such small amounts of data are associated with the *cleanest* background clusters, the multiple-site GLMM technique is advantageous compared to other techniques because it borrows statistical strength from the multiple site data. In other words, incorporating the between-site covariance within a region not only compensates for the potential problem of small data sets but also improves the statistical power to detect small changes. The GLMM time series model and statistical details can be found in Chan (2009).

Temperature effects were accounted for in the results shown in Table 2 and Fig. 10 by using daily 1-h maximum observation as the covariate in the time series model. In some regions, the temperature adjustment resulted in a switching of trend directions but neither the unadjusted or adjusted trends were statistically significant. In general, the temperature adjustment tended to result in reductions in the magnitude of the summer (JJA) trends only, with no systematic reduction or increase in the other seasons. This suggests that the temperature trend varied in the same direction as the ozone trend during the most photochemically active months. It is therefore, important that the temperature effects be removed in the ozone variations in the summer, but not necessarily in the other seasons.

The results of the long-term trend analyses are not straightforward because the regions and the direction of the trends vary from season to season. The major results can be summarized as follows:

- In the Pacific coastal regions of southwestern British Columbia (Canada) and California (US), the decadal trends were increasing in all seasons except fall (SON) in California. The trends were statistically significant in British Columbia in all seasons except the fall, but were not significant in California in any seasons.
- In the Atlantic coastal zone of southern New Brunswick and southern Nova Scotia (Canada) and northeast Maine (US), the trends were positive (but significantly so only in the spring), except in the winter when the trend was negative (but not significant). Hence, the only significant trend detected was an upward trend in the

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spring.

- The eastern part of Canada and the US (i.e., east of Lake Superior in Canada and east of the Mississippi River in the US), showed negative trends in all regions in all seasons, with three exceptions: 1) the insignificant positive trends in Atlantic Canada/northeast Maine in the summer, fall and winter (discussed above), 2) a significant positive trend in winter (DJF) at sites located in the US Midwest (Ohio, Indiana and Illinois), and 3) significant positive trends at all sites in Quebec (Canada) and one site in Vermont (US) during the summertime.
- At all sites all central/western Canada and the US, the trends tended to be negative in the spring and fall but positive in the summer and winter. It is worth noting however, that the density of the sites in the central and western regions was very low – meaning that the representativeness of the regions was considerably lower than for regions in the east.

Although the individual regional trends are difficult to interpret, collectively they exhibit similar tendencies over large areas of North America. For example, the Pacific and Atlantic coastal regions of Canada and the US generally exhibit positive trends while the continental regions of central/western Canada and the US tend to exhibit negative trends in the spring and fall and positive trends in the summer and winter. This is consistent with previously published studies at background and/or free troposphere sites that documented increasing trends in mixing ratios, particularly in the winter and spring months, over the last two decades (Jaffe et al., 2003, 2007; Lelieveld et al., 2004; Jonson et al., 2006; Oltmans et al., 2006; Derwent et al., 2007; Parrish et al., 2009).

In contrast, the regions in the high NO_x and NMHC emission areas of eastern Canada and the eastern US (i.e., PC2, PC3 and PC4 in the SON map of Fig. 10) show consistent negative trends in all seasons, with the steepest trends occurring in the summer. In the US, this is consistent with, and expected from, the major ozone season (May through September) decreases in NO_x emissions in those areas during



the period 2000 to 2007 (Canada–United States, 2008). This again implies that these regions are not continentally or hemispherically representative.

The explanation of background ozone trends is not simple. Possible reasons include rising NO_x emissions from developing nations and higher CO and NO_x emissions from large scale forest fires. The latter might be a plausible explanation for the positive ozone trends found along the west coast (Fig. 10) in that biomass fires that burned a large area of Siberia in the summer of 2003 and were transported to the west coast of North America, were the largest in at least 10 years (Jaffe et al., 2004). This illustrates the point that because of the slowly-varying nature of the background, the importance of this signal can easily be masked by any major regional-scale ozone signals.

5 Summary and conclusions

This study provided a comprehensive analysis of decadal, seasonal and diurnal temporal variations of background ozone in different chemical regimes over Canada and the US for the first time. Background ozone mixing ratios for North America were estimated from measurements taken at 97 non-urban sites covering most of the landmass of Canada and the US from 24° N to 56° N and 65° W to 123° W (with altitudes ranging from 2 to 3178 metres) for days with air mass trajectories from the *cleanest* of 6 trajectory clusters at every site. As expected from the literature, the seasonal background ozone variations in most of the regions (mainly in Canada) located away from the major precursor emission sources yielded a single spring maximum (Fig. 8a). The results indicate that, as one would expect, a single *background* ozone level cannot be defined for all of North America. Rather, background ozone, as defined here, varied geographically and seasonally. As previously published by Parrish et al. (2009) and Jaffe et al. (2007), it was found that sites in coastal regions (coasts of the Pacific and Atlantic Oceans), background levels are predominantly influenced by flow off the oceans, while in continental areas, *background* levels are predominantly influenced by flow from the north.

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Those continental areas of Canada having few anthropogenic precursor emission sources to the north of the measurement sites (e.g. PC11, i.e., northwestern Ontario, Canada) were found to have background levels considerably lower than in the continental areas where large anthropogenic precursor emission sources do exist (e.g. PC4, i.e., Ohio River Valley, southeastern US). For example, the mixing ratios annually ranged from 21 to 38, and 23 to 38 ppb for continental Eastern Canada (PC1, PC6, and PC11) and Eastern US (PC2, PC3 and PC4), respectively. The Pacific (coastal Western Canada, PC10) and Atlantic (coastal Eastern Canada, PC5) coastal regions typically had lower background levels, ranging from 14 to 24, and 17 to 36 ppb, respectively. The regional disparities of the background levels suggest that the term *background* for the heavily source-affected areas does not represent the same *background* as for the coastal or low-pollution-impacted continental areas of North America. Sites that are in close proximity to high NO_x and isoprene emission sources, even for non-urban sites, are shown to be impacted by regional pollution and are therefore not representative of the continental background.

Background ozone levels varied seasonally in all regions. For example, the mixing ratios ranged from 31 to 38 in MAM (28 to 38 in DJF), and 33 to 38 (24 to 33) ppb for continental Eastern Canada and Eastern US, and from 22 to 24 (15 to 23) and 39 to 44 (35 to 39) ppb for coastal Western Canada and coastal Western US, respectively. The background ozone estimates calculated in this study provides more detailed seasonal and diurnal information for different regions compared to previously-published results and at the same time, these estimates fall within those published values for North America, ranging from 15 to 45 ppb (Trainer et al., 1993; Altshuller and Lefohn, 1996; Lin et al., 2000). Additionally, seasonal and diurnal cycles calculated from this study are consistent with those in other locations outside of North America (Logan, 1985; Vingarzan, 2004; Oltmans et al., 2006), for example, in Greenland (Helmig et al., 2007), Ireland (Derwent et al., 2006), Japan (Pochanart et al., 2002), and China (Xu et al., 2008).

Decadal trends increased in regions along the Pacific coast in all seasons; however,

trends decreased in most of the eastern US and eastern Canada in all seasons. For example, PC10 (Pacific Canada) had an increase of 0.28 ppb/a compared to PC2 (eastern US) which had a decrease of 0.59 ppb/a. Note that this is a net decrease. Thus, the actual regional decrease might have been greater without the increase in background. These results emphasize the important impact of regional and/or local ozone precursor control efforts regardless of the slowly-varying (increasing) background. As shown in this observation-based study, the importance of background ozone appears to be offset in continental areas due to the large scale regional decrease of ozone in the planetary boundary layer through numerous ozone precursor emission reduction programs over the last decade (Canada–United States, 2008; US EPA, 2007). However, the relative importance of the background may increase in the future if the background continues to rise.

The main messages from this study are as follows:

- Increasing trends were observed along the Pacific coast of Canada and the US in all seasons, although the trends in California were not statistically significant. The statistically significant, temperature-adjusted ozone decadal trends in British Columbia, Canada increased at a rate of 0.28 ± 0.26 , 0.72 ± 0.55 , and 0.93 ± 0.41 ppb/a in MAM, JJA, and DJF, respectively. If one assumes that the west coast increasing trends are representative of the hemispheric background, then it follows that, in the eastern US, the widespread decreasing trends observed in all season must be due to regional ozone decreases caused by decreases in ozone precursor emissions since the mid-2000s, e.g., the greatest decrease of the temperature-adjusted ozone trend among all eastern regions was -1.56 ± 0.45 ppb/a (PC3 in JJA). This implies that our estimated *background* ozone levels for the eastern US are not truly representative of hemispheric background levels but rather of hemispheric-plus-regional background levels. This is reflected in the shape of the seasonal cycles for eastern US regions (Fig. 8a) which show a strong summertime maximum that can only be explained by regional-scale photochemical production of ozone.

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- The similarity of the seasonal variations and the narrow ranges of variabilities over such large regions, particularly in the low pollution impacted regions of PC1, PC5, PC6, PC11, PC8 and PC10 as defined by PCA/JJA, the method developed here provides confidence in the selection of representative background air, with minimal influence of the any regional photochemical signals. This evidence also suggests that the background ozone mixing ratios teased out from the entire non-urban data set are spatially consistent and continental (possibly hemispheric) in nature.

Appendix A 2002 simulation annual run using a CTM (Moran, 2009)

The ambient mixing ratios of NO_x and isoprene were predicted using version 1.3.1 of Environment Canada (EC)'s unified regional air quality modelling system (AURAMS) (Gong et al., 2006). The AURAMS AQ modelling system consists of three main components: (a) a prognostic meteorological model, GEM; (b) an emissions processing system, SMOKE; and (c) an off-line regional chemical transport model (CTM), the AURAMS CTM. Each of these three components and the specific configurations chosen for the 2002 annual simulation are briefly described in turn.

The Global Environmental Multiscale (GEM) meteorological model is an integrated weather forecasting and data assimilation system that was designed to meet Canada's operational needs for both short- and medium-range weather forecasts (Côté et al., 1998A,B; Mailhot et al., 2006). For the 2002 simulation, GEM version 3.2.0 with physics version 4.2 was run on a variable-resolution North American regional horizontal grid. The grid consisted of a 353×415 horizontal global grid on a rotated latitude-longitude map projection. The grid spacing on the 270×353 uniform regional "core" grid was approximately 24 km (0.22°), and the 28 vertical hybrid-coordinate levels reached from the Earth's surface to 10 hPa. A model time step of 450 s was used.

The Sparse Matrix Operator Kernel Emissions (SMOKE) processing system is an emissions processing system that is used to create files of temporally disaggregated,

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spatially disaggregated, and chemically speciated emissions for various CTMs from national criteria-air-contaminant (CAC) emissions inventories (e.g., Houyoux et al., 2000; CEMPD, 2007). Version 2.2 of SMOKE (<http://www.smoke-model.org/index.cfm>) was used to prepare the very large set of day-specific emission files needed for the 2002 simulation. The three national anthropogenic emission inventories that were processed by SMOKE to prepare input emission files for AURAMS were (a) the 2000 Canadian CAC emission inventory, (b) the 2001 US CAC emission inventory, and (c) the 1999 Mexican CAC emission inventory. Each of these inventories contained emissions of seven CAC species: SO₂; NO_x; CO; NH₃; VOC; PM_{2.5}; and PM₁₀.

The AURAMS chemical transport model is a multi-pollutant, regional CTM that was developed by EC as a tool to study the formation of PM, ozone, and acid deposition in a single “unified” framework. For the 2002 simulation, AURAMS version 1.3.1 was run on a 150 by 106 uniform, continental-scale North American regional horizontal grid on a secant polar-stereographic map projection true at 60° N. The grid spacing was 42 km (Fig. 3). 28 vertical modified Gal-Chen levels reached from the Earth’s surface to 29 km. A model time step of 900 s was used, and AURAMS-predicted fields were output once an hour. Finally, the figures (Figs. 3 and 4) are the seasonal domain-average mixing ratio fields for the ambient mixing ratios of NO_x and isoprene aggregated from the hourly outputs.

Acknowledgement. Thanks are due to Pierrette Blanchard (Environment Canada/Science and Technology Branch, Toronto, Canada) for scientific advice, Michael Moran (Environment Canada/Science and Technology Branch, Toronto, Canada) for descriptions of AURAMS, Michael Shaw (Environment Canada/Science and Technology Branch, Toronto, Canada) for many SAS/GRAPH[®] software’s macros and subroutines, Jacinthe Racine (Environment Canada/Science and Technology Branch, Montreal, Canada) for performing numerous and complicated trajectory calculations, and Qiong Zheng (Environment Canada/Science and Technology Branch, Toronto, Canada) for producing the NO_x and isoprene mixing ratio fields using AURAMS.

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Table 1. Summary of background ozone seasonal variations **(a)** and diurnal variations **(b)** by season (in ppb) for a given region. The ranges are calculated for seven regions separately, i.e. coastal/continental Eastern Canada, continental Eastern US, coastal/continental Western Canada, and coastal/continental Western US. The groupings of sites are based on the principal component analysis for the JJA months.

(a) Region	Annual	Seasonal ranges			
		MAM	JJA	SON	DJF
Eastern Canada (east of 98° W)					
– coastal (PC5)	17–36	28–36	17–27	17–26	26–36
– continental (PC1, PC6 and PC11)	21–38	31–38	21–31	21–28	28–38
Eastern US (east of 98° W)					
– continental (PC2, PC3, and PC4)	23–38	33–38	27–37	23–27	24–33
Western Canada (west of 98° W)					
– coastal (PC10)	14–24	22–24	15–22	14–15	15–23
– continental (PC8)	20–36	32–36	21–32	20–24	24–35
Western US (west of 98° W)					
– coastal (PC12)	35–44	39–44	39–44	35–39	35–39
– continental (PC7 and PC9)	40–51	48–51	44–51	40–44	40–48
(b) Region	Annual	Diurnal ranges by season			
		MAM	JJA	SON	DJF
Eastern Canada (east of 98° W)					
– coastal (PC5)	13–39	30–39	13–30	16–26	29–33
– continental (PC1, PC6 and PC11)	15–42	32–42	15–31	18–27	29–33
Eastern US (east of 98° W)					
– continental (PC2, PC3, and PC4)	18–46	29–46	19–45	18–33	23–30
Western Canada (west of 98° W)					
– coastal (PC10)	10–32	16–32	10–25	13–18	18–20
– continental (PC8)	15–44	28–44	15–36	16–26	27–31
Western US (west of 98° W)					
– coastal (PC12)	27–51	36–51	27–51	31–42	37–45
– continental (PC7 and PC9)	37–55	48–54	38–55	32–38	41–44

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Table 2. Decadal trends modelled by GLMM using daytime (12:00–18:00 LST) average ozone mixing ratios from 1997 to 2006 by season. Only regions with significant trends (p -value less than 0.05) are shown.

PC	Season	p -value ^a	Temp-adjusted trend (ppb/a)	Non-adjusted trend (ppb/a)	ABS (Temp-adjusted trend) minus ABS (Non-adjusted trend) (ppb/a)
1	MAM	0.0002	-0.18±0.1	-0.15±0.1	0.03
2		<.0001	-0.59±0.14	-0.61±0.14	-0.02
3		0.0003	-0.66±0.27	-0.63±0.22	0.03
5		<.0001	-0.21±0.05	-0.18±0.05	0.03
6		0.0459	0.34±0.34	0.32±0.34	0.02
7		0.008	-0.61±0.45	-0.03±0.47	0.58
10		0.0391	0.28±0.26	0.29±0.3	-0.01
12		0.0215	-0.5±0.39	-0.59±0.33	-0.09
1	JJA	0.0005	0.27±0.15	0.37±0.18	-0.1
2		<.0001	-0.97±0.22	-1.08±0.23	-0.11
3		<.0001	-1.56±0.45	-1.81±0.42	-0.25
4		<.0001	-0.89±0.24	-0.91±0.19	-0.02
8		0.0196	0.38±0.3	0.64±0.24	-0.26
9		0.0119	0.55±0.43	0.58±0.44	-0.03
10		0.0136	0.72±0.55	0.82±1.98	-0.1
1	SON	0.0228	-0.12±0.1	-0.12±0.1	0
2		<.0001	-0.45±0.16	-0.39±0.22	0.06
3		<.0001	-0.74±0.29	-0.91±0.3	-0.17
8		0.0079	-0.39±0.29	-0.61±0.31	-0.22
5	DJF	0.0006	0.7±0.39	0.58±0.38	0.12
6		0.0361	0.66±0.61	1.01±0.62	-0.35
7		<.0001	0.93±0.41	0.88±0.41	0.05

^a p -values are shown for temperature-adjusted trends only.

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Table 3. A comparison of the statistical methods used and the background ozone trend estimates focusing on Western Canada and US from three recent papers and this paper.

Authors	Period	Location	Average metrics	Data screening method	Statistical method	Season	Trend estimate (ppb/year)
Oltmans et al. (2008)	1988–2007, 1999–2007	Western US	Daytime averages	Backward trajectory	Autoregressive model – a cubic polynomial for trend	Winter Spring Summer Fall	No significant changes
Jaffe et al. (2007)	1987–2004	Western US (Rocky Mt., Yellowstone, Lasseon)	Daytime monthly means	N/A	Linear regression	Winter Spring Summer Fall	+0.21 to +0.62 +0.33 to +0.59 +0.43 to +0.50 +0.28 to +0.56
Parrish et al. (2009)	Various length covering (1974–2007)	West coast of the US	Monthly means	Local wind data	Linear regression	Winter Spring Summer Fall	+0.43±0.17 +0.46±0.13 +0.24±0.16 +0.12±0.14
This paper	1997–2006	Western Canada and the US	Daytime averages	Backward trajectory	Regional trend analysis using GLMM – long-term sinusoidal cycles (3 to 5 years) for trend	DJF (PC7) MAM (PC10) JJA (PC10) SON (PC9)	+0.93±0.41 +0.28±0.26 +0.72±0.55 No significant changes

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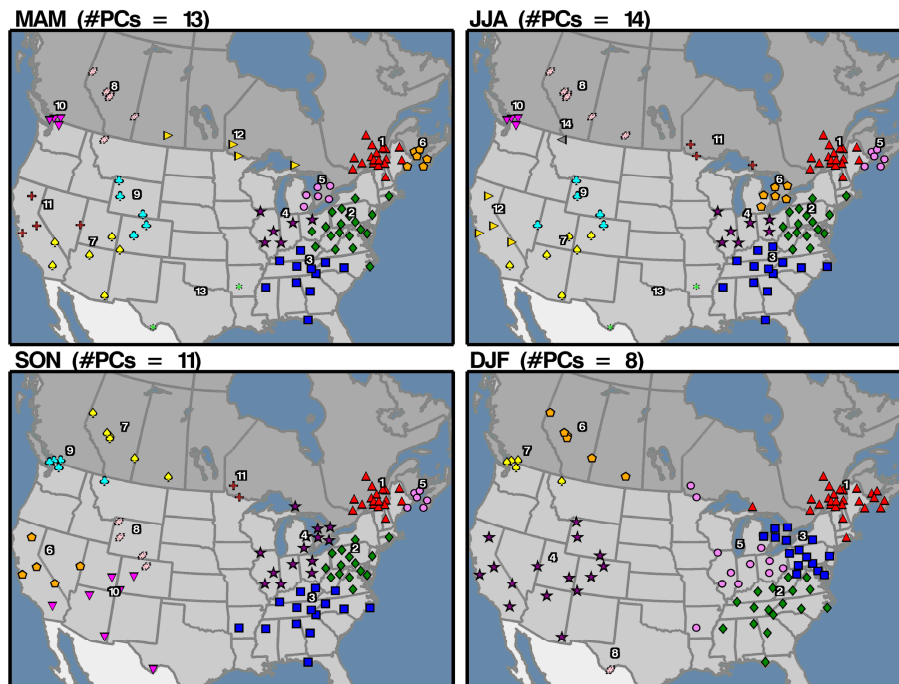


Fig. 1. Results of rotated PCA analysis using six-hour ozone averages for the period 1997–2006 for different seasons. The number of regions in the season is shown in the bracket on top of each panel. The seasonal breakdowns are as follows: spring (MAM), summer (JJA), fall (SON), and winter (DJF).

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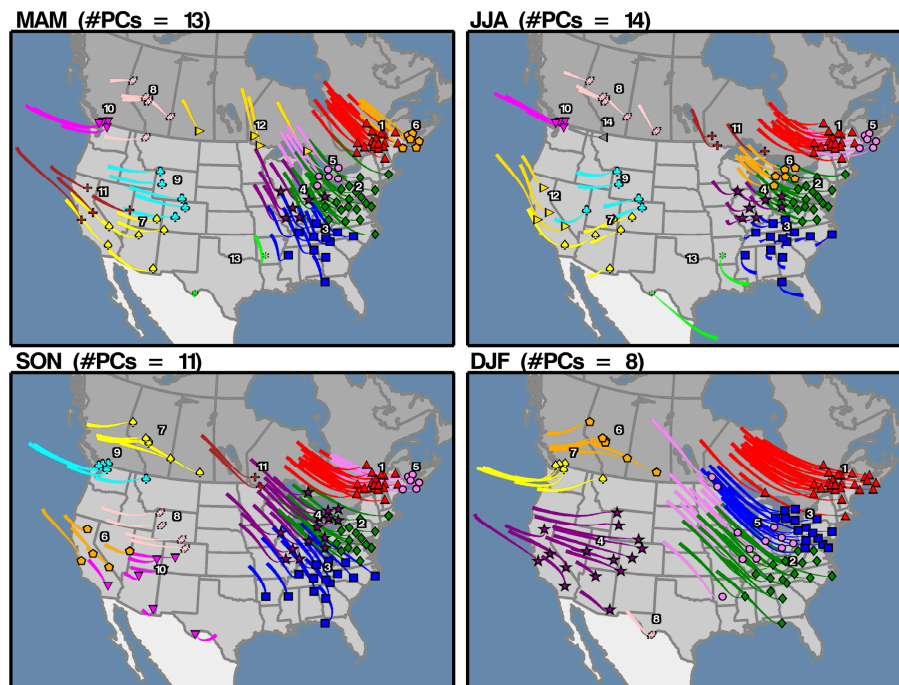


Fig. 2. Average three-day backward air parcel trajectories for each ozone measurement site for the period 1997–2006 for different seasons.

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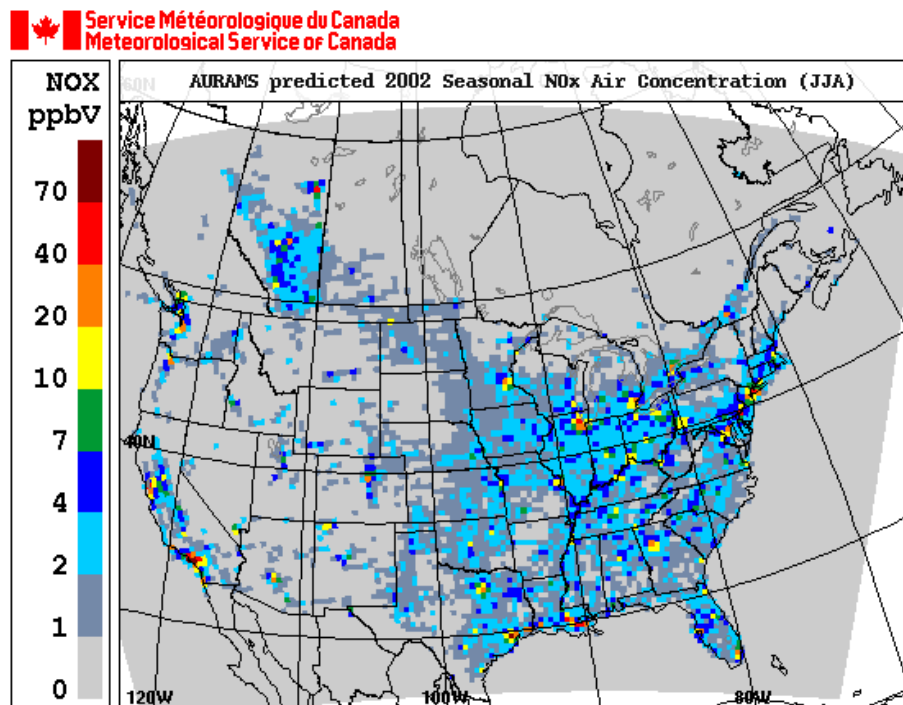


Fig. 3. AURAMS-predicted seasonal-average mixing ratios of ambient NO_x for summer (JJA).

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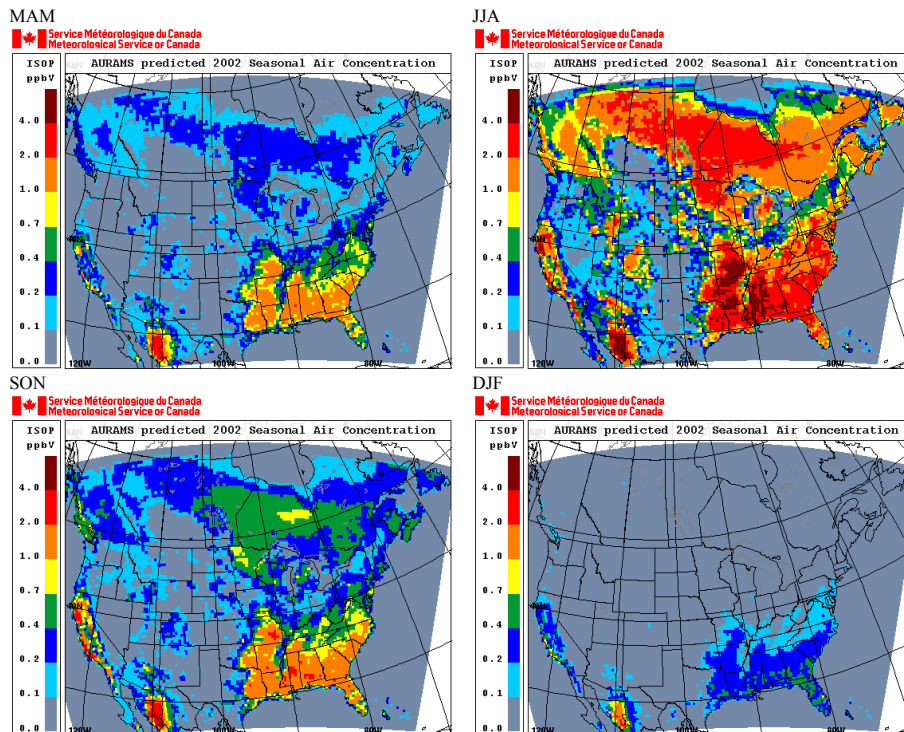


Fig. 4. AURAMS-predicted seasonal-average mixing ratios of ambient isoprene for spring (MAM), summer (JJA), fall (SON) and winter (DJF).

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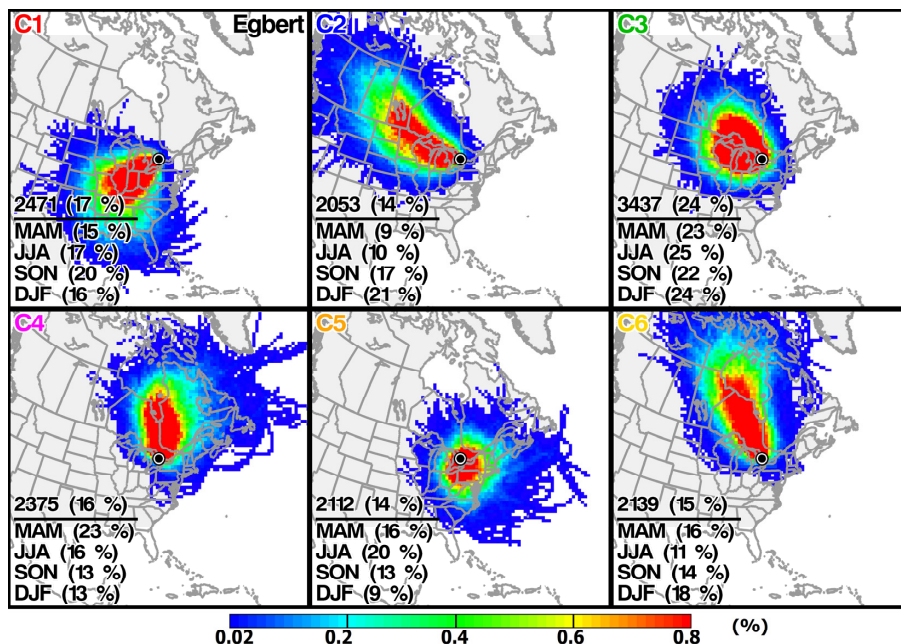


Fig. 5a. Probability density plots of background trajectory for Egbert ($44^{\circ}13'57''$ N, $79^{\circ}46'53''$ W), located in Ontario, Canada. Trajectory clusters are shown as probability density plots whereby the blue-to-red colors in the grid squares represent the relative frequency with which trajectories passed over the grid squares (calculated as the number of trajectories in the cluster passing over a grid square divided by the total number of trajectories passing over all grid squares in all clusters). Shown only are the grid cells with probability greater than 0.02. Those grid cells with probability greater than or equal to 0.8 are shown with the same color.

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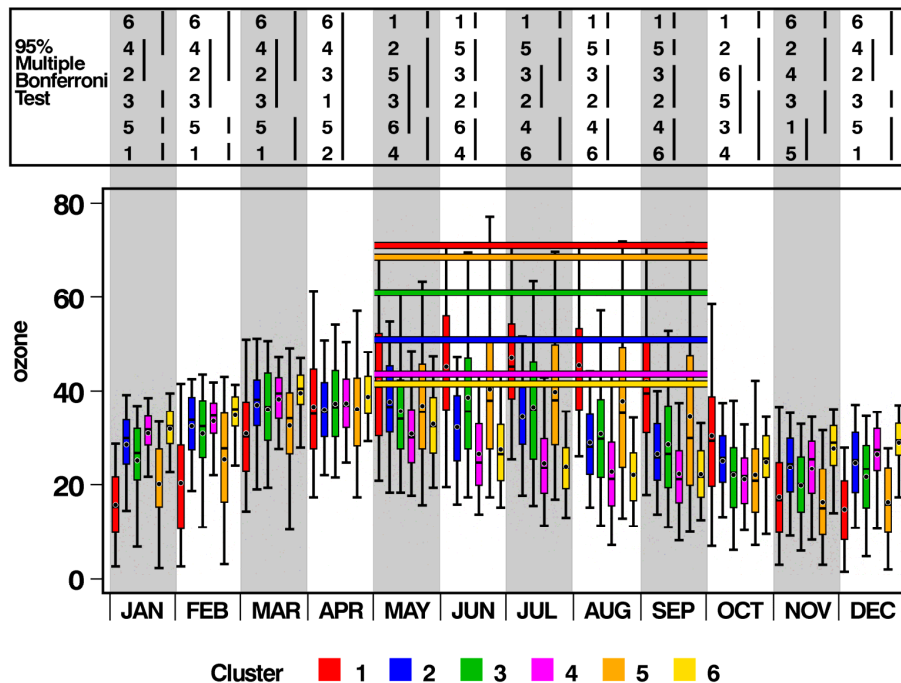


Fig. 5b. Monthly box-and-whisker plot of the six-hour-average ozone mixing ratios associated with the trajectory clusters in Fig. 5a. The endpoint of the upper whisker, upper edge, dot inside, line inside, lower edge of the box and endpoint of the lower whisker show the 95th, 75th, mean, median, 25th and 5th percentiles, respectively.

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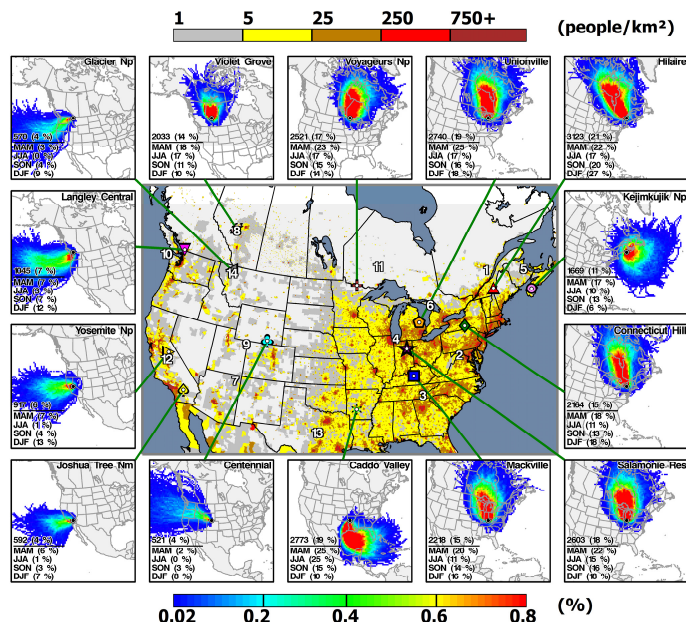


Fig. 6a. Probability densities of air parcel trajectory clusters (*cleanest* background air) associated with the lowest May–September 95th percentile ozone mixing ratios for 14 statistically representative sites (out of 97 in total) for the years 1997–2006 combined. The total number of trajectories for the cluster and the transport frequency (in bracket, %) is shown above the horizontal bar. The relative seasonal transport frequencies (relative to other five clusters) are shown below the bar (other five clusters not shown). The gridded population shown in the centre was obtained from the Centre for International Earth Science Information Network (CIESIN), Columbia University; and Centro Internacional de Agricultura Tropical (CIAT), Gridded Population of the World (GPW), Version 3, for the year 2005. Palisades, NY: CIESIN, Columbia University. Available at: <http://sedac.ciesin.columbia.edu/gpw>.

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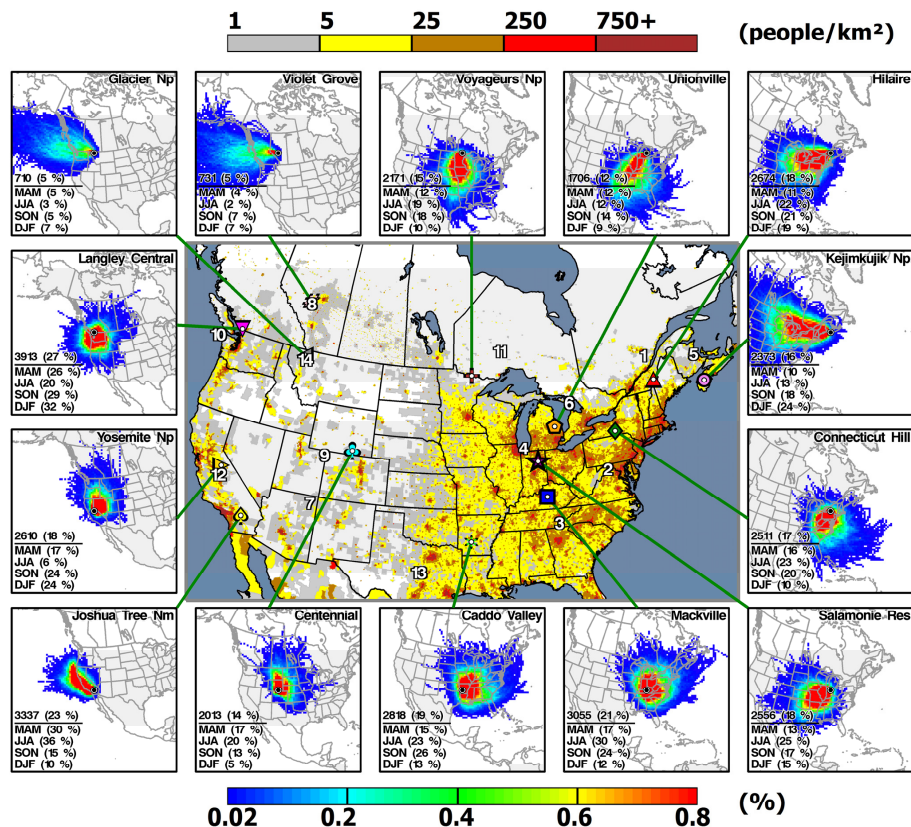


Fig. 6b. Probability densities of air parcel trajectory clusters (*most polluted* air) associated with the highest May–September 95th percentile ozone mixing ratios for 14 statistically representative sites (out of 97 in total) for the years 1997–2006.

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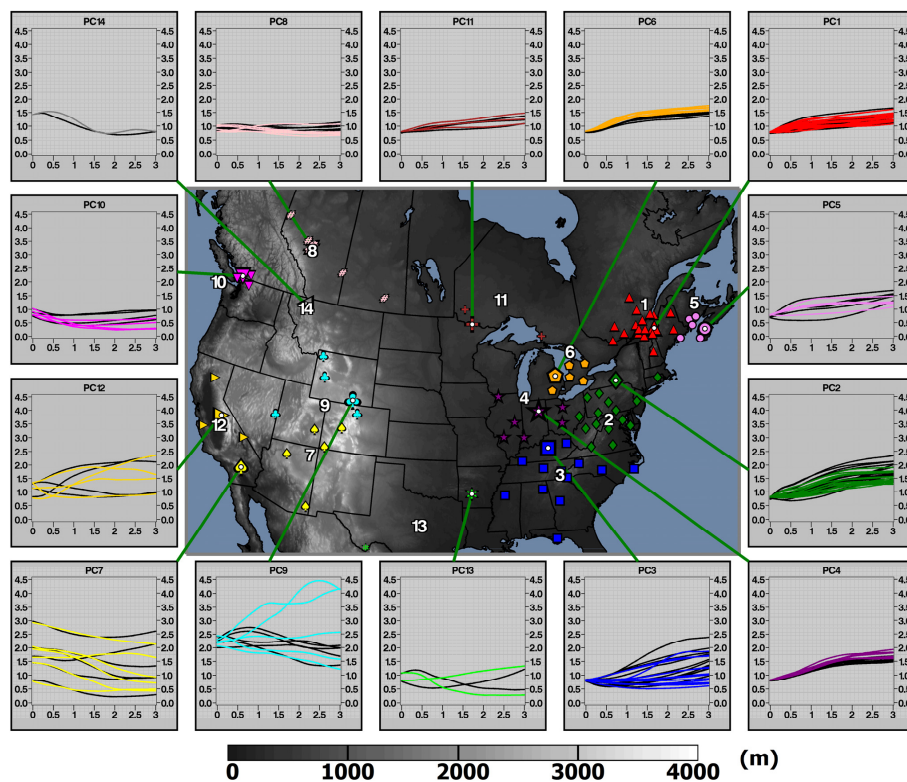


Fig. 7a. Mean summer (JJA, color) and winter (DJF, black) trajectory transport heights (ASL, km) associated with the *cleanest* air cluster grouped by rotated PCA for the JJA months. Figure shows the transport height from zero to three days prior to arrival at the site.

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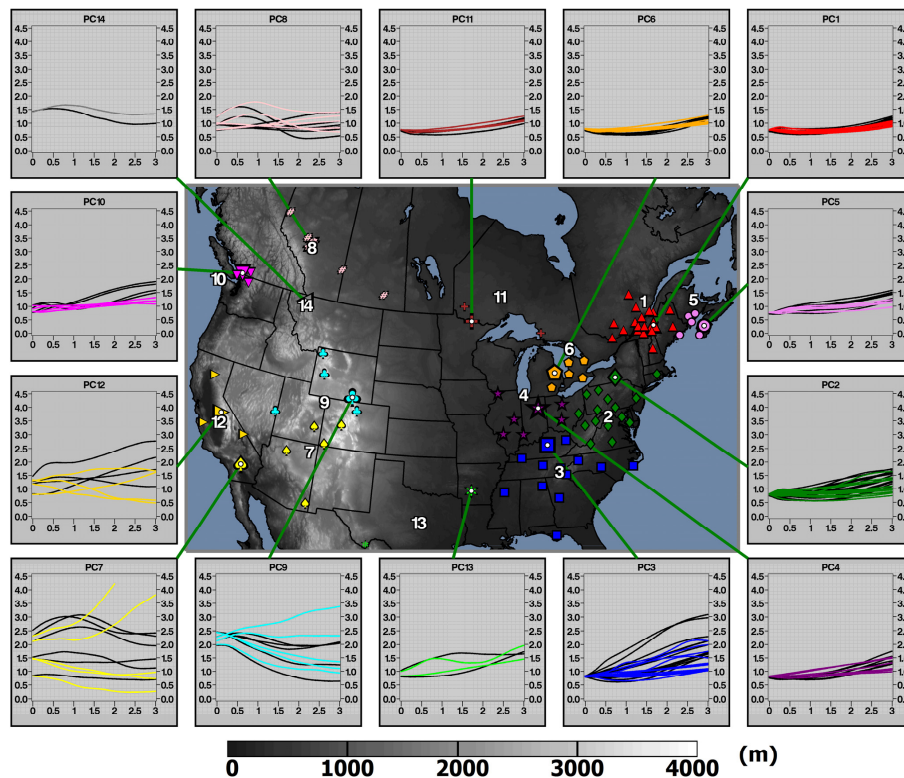


Fig. 7b. Mean summer (JJA, color) and winter (DJF, black) trajectory transport heights (ASL, km) associated with the *most polluted* air cluster grouped by rotated PCA for the JJA months. Figure shows the transport height from zero to three days prior to arrival at the site.

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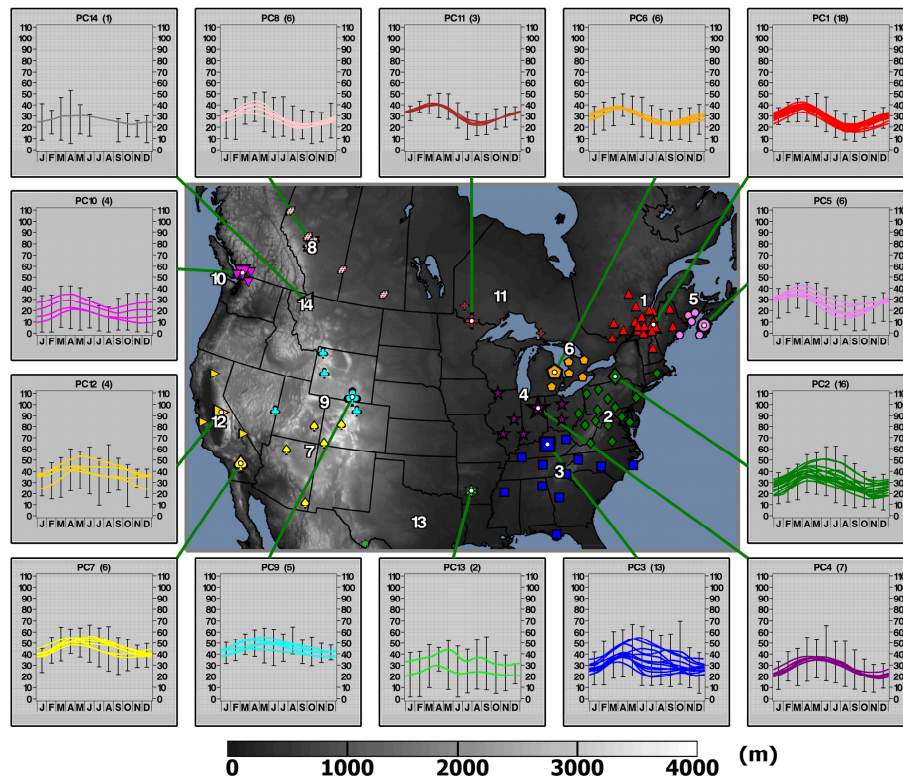


Fig. 8a. Seasonal ozone variations generated by LOWESS (see text) associated with the *cleanest* air trajectory clusters for all 97 sites. The error bars show the monthly ensemble site 5th to 95th percentiles for the region. The regional groupings are based on rotated PCA for JJA months. Elevations (above sea level, metres) are shown in gray scale from dark to light to represent low to high elevations. Elevations have been normalized to have a minimum of zero metre.

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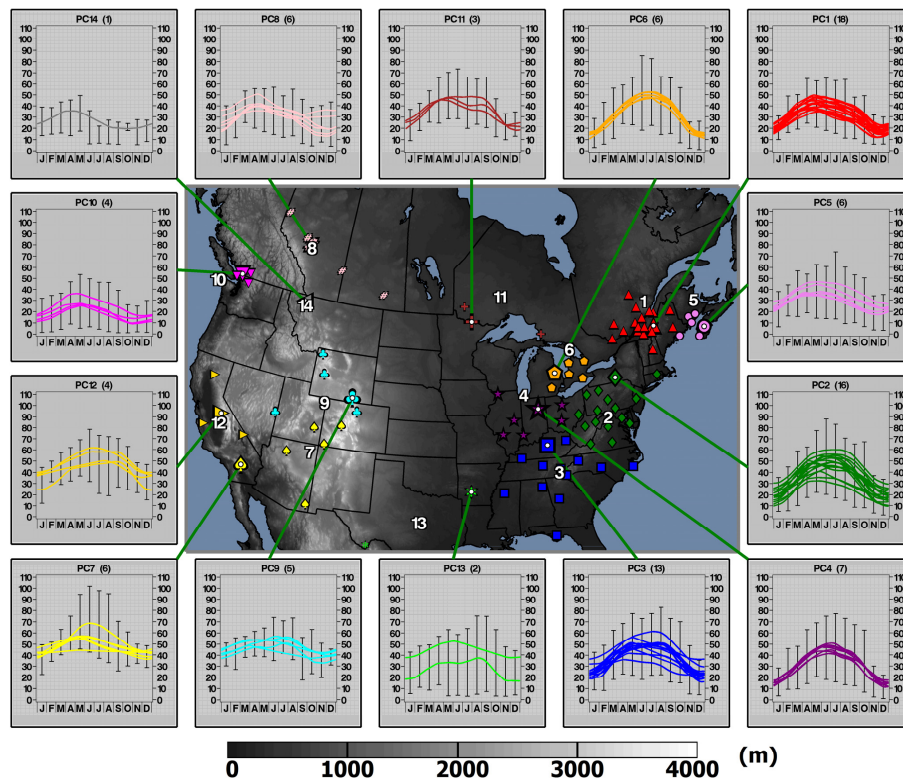


Fig. 8b. Seasonal ozone variations associated with the *most polluted* air trajectory clusters for all 97 sites.

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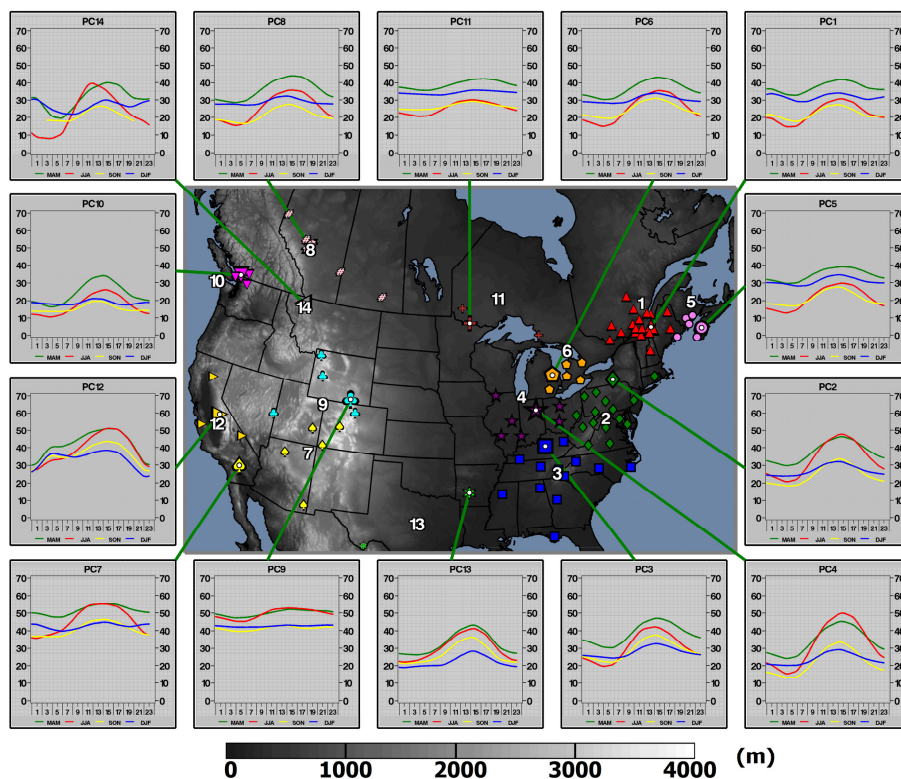


Fig. 9a. Seasonally averaged ozone diurnal variations associated with the *cleanest* air trajectory clusters grouped by rotated PCA for JJA months.

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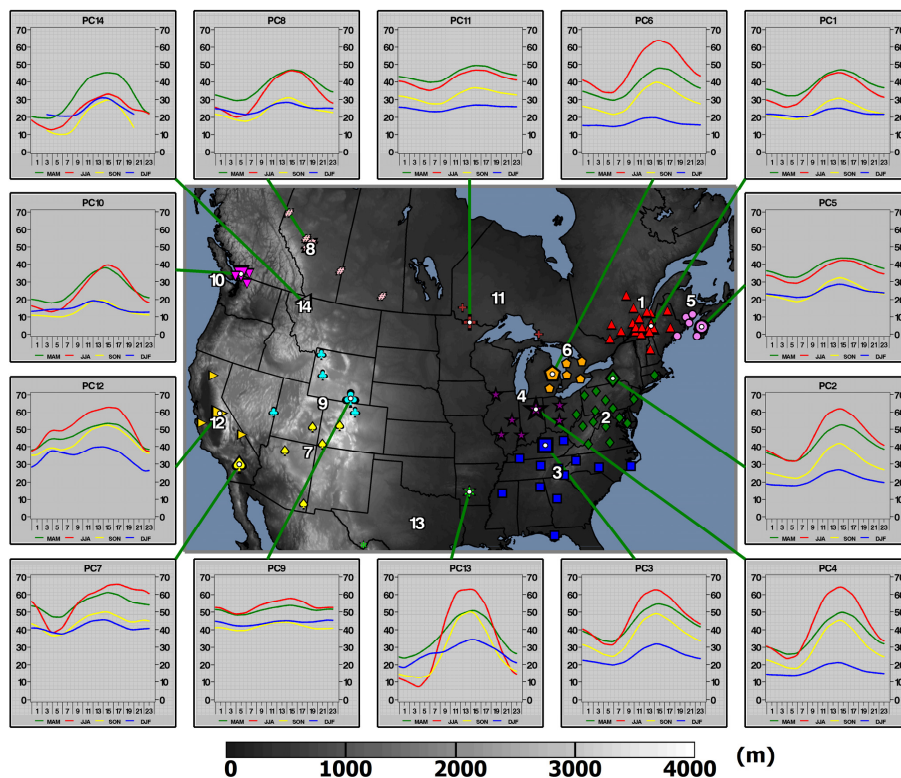


Fig. 9b. Seasonally averaged ozone diurnal variations associated with the *most polluted* air trajectory clusters grouped by rotated PCA for JJA months.

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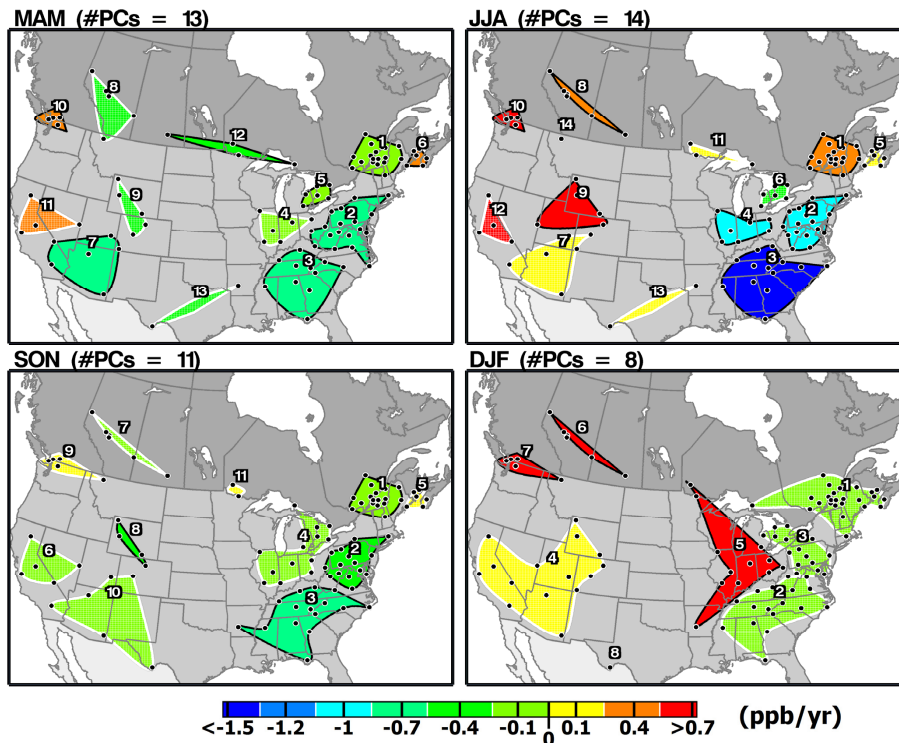


Fig. 10. Regional decadal trends of daytime (12:00–18:00) average ozone mixing ratios associated with the *cleanest* air, modelled by GLMM for different seasons. Regions have been previously defined by rotated PCA for different seasons. Significant trends at the 0.05 level are shown with a black regional boundary. No evidence of statistical significance is shown with a white boundary.

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