Interannual variability of ozone and carbon monoxide at the Whistler high elevation site: 2002-2006

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Abstract

In spring 2002, an atmospheric measurement site was established at the peak of Whistler Mountain in British Columbia, Canada to measure trace gases, particle chemistry and physics, and meteorology. This paper uses continuous measurements from March 2002 to December 2006 to investigate the influence of trans-Pacific transport and North American forest fires on both O_3 and CO at Whistler. Annual mean mixing ratios of O_3 and CO were 41 ppbv (monthly means of 35-48 ppbv) and 145 ppbv (monthly means of 113-177 ppbv) respectively with both species exhibiting an annual cycle of late-winter to early-spring maxima and summer minima. The absence of a broad summer O_3 peak differs from previously-reported high altitude sites in the western US. The highest monthly-averaged O_3 and CO mixing ratios relative to the 5-year monthly means were seen in fall 2002 and spring 2003 with increased O_3 and CO of 10% and 25% respectively. These increases correspond to anomalously-high values reported at other Northern Hemisphere sites and are attributed to fires in the Russian Federation. Air mass back trajectory analysis is used to associate the mean enhancements of O_3 and CO with trans-Pacific transported or North American air masses relative to the Pacific background. Mean values of the enhancements for March to June in trans-Pacific air masses were 6 ppbv and 16 ppbv for O_3 and

CO respectively. In summers 2002-2006, higher CO and O_3 mixing ratios were almost always observed in North American air masses and this relative enhancement co-varied for each year with the western US and Canada total wildfire area. The greatest enhancements in O_3 and CO were seen in 2004, a record year for forest fires in Alaska and the Yukon Territory with average O_3 and CO mixing ratios 13 and 43 ppbv above background values.

1 Introduction

Factors affecting lower tropospheric ozone are important for the development of policies for local and regional pollution control as well as for evaluating the effectiveness of these controls. Ozone is both a constituent of smog and a greenhouse gas, and it plays a role in controlling the oxidizing capacity of the troposphere. Tropospheric ozone (O_3) is formed primarily by the oxidation of carbon monoxide (CO) and non-methane hydrocarbons (NMHCs) in the presence of nitrogen oxides (NOx). Emissions of ozone precursors are from both anthropogenic and biogenic sources. NMHCs are emitted from vegetation, fossil fuel combustion, and manufacturing; major sources of NOx include fossil fuel burning, lightning, emissions from the biosphere, and stratospheric injections. Biomass burning is also a significant source of CO, NMHCs and NOx (Crutzen and Andreae 1990; Galanter et al., 2000; Simpson et al., 2011) and during the boreal fire season has been shown to influence regional ozone in North America (Wotawa and Trainer, 2000; McKeen et al., 2002).

On the west coast of North America, the contribution to regional ozone of trans-Pacific transported ozone and its precursors also needs to be considered. Over the past two decades, observational and modelling studies have shown that particle and trace gas concentrations throughout the northern hemisphere are influenced by intercontinental and hemispheric transport. Trans-Pacific transport of pollutants was first recognized as an issue in the late 1980s and early 1990s (Andreae et al., 1988; Kritz et al., 1990). Since then, numerous studies have documented pollution reaching the west coast of North America resulting in increases in ground level particles, O_3, CO, and pesticides (e.g. Husar et al., 2001; Jaffe et al., 2003; Bailey et al., 2000; Singh et al., 2009 and references therein). Jaffe et al. (1999) showed that transport of pollutants across the Pacific could have an impact on ground-level ozone in the Western US. Modelling

studies have furthered the understanding of how transport may affect overall air quality and chemistry on the west coast of North America. Pollution crossing the Pacific Ocean was estimated to increase CO over western US by up to 25% (Liang et al, 2004; Stohl et al., 2002). Anticipated three-fold increases in Asian industrial emissions from 1985 – 2010 were calculated to result in a 2-6 ppbv increase in ground-level ozone in the western US (Jacob et al., 1999).

To understand the factors affecting O_3 budgets, comparisons of O_3 with CO have been made in North American outflow and also at sites on the west coast of the US (Parrish et al., 1998; Weiss-Penzias et al., 2004; Honrath et al., 2004; Val Martin et al., 2006). The basis for the CO and O_3 comparison is the assumption that CO mixing ratios are directly related to CO and O_3 precursor emissions such as non-methane hydrocarbons and nitrogen oxides, and that changes in CO are indicative of changes in O_3 precursor species and thus would exhibit a relationship with net ozone production (Parrish et al., 1993; Parrish et al., 1998; Honrath et al., 2004). Annual and interannual variability in CO is strongly dependent on both fossil fuel emissions and biomass burning (Novelli et al., 2003; Wotawa et al., 2001; Yurganov et al., 2005).

Trends in background ozone have been identified for several sites in western North America. Jaffe and Ray (2007) have examined 20 years of data (1987 – 2004) and found an average increase of 0.26 ppbv/year of O_3. Parrish et al., (2009) have found a similar trend from looking at west coast marine boundary layer sites (0.34 ppbv/year). Chan and Vet (2010) used a muti-site cluster analysis and also found a significant upward trend in background ozone along the west coast of North America. Similar trends have been identified in free tropospheric measurements through a comprehensive integration of data from multiple years and west coast studies (Cooper et al., 2010). Reasons for these trends are unclear and several possibilities have been suggested including regional continental or ship emissions, biomass burning and trans-Pacific transport (Cooper et al., 2010; Jaffe and Ray 2007; Dalsoren et al., 2010; Jaffe, 2010).

Relationships between O_3 and CO in North America over multiple years have mostly been made at ground-level sites (e.g. Parrish et al., 1998). Although transport of pollutants is observed at ground-level sites, significant transport occurs in the free troposphere and therefore, the frequency of observable transport events should increase at a high elevation site (VanCuren and Cahill, 2002). In addition, measurements in the free troposphere, largely unaffected by local emissions, are valuable to understand the regional and long-range emission and transport

influences. Most coupled CO and O_3 data from the free troposphere come from aircraft campaigns which often include a detailed suite of measurements with good spatial coverage but are of limited time duration. Major field campaigns over the Pacific since the early 1980s have provided coupled CO and O_3 measurements (e.g Talbot et al., 1994; Heald et al., 2003; Bertschi et al., 2005; Liang et al., 2007). Satellite observations also expand the spatial and temporal scale of both emission and transport of pollutants. In particular, the integration of satellite, aircraft, and ground-based measurements furthers the understanding of processes related to transportation and transformation of pollutants (e.g. Zhang et al., 2008).

High elevation surface sites in western North America can provide long-term measurements in the lower free troposphere. Long-term records of ozone are available from several US National Park sites with varying degrees of influence from regional pollution (Jaffe and Ray, 2007). The Mt Bachelor site in central Oregon (Weiss-Penzias et al., 2004) is well situated for background free-tropospheric chemistry and atmospheric measurements began there in spring 2004.

In March 2002, Environment Canada began measurements of particles and some trace gases at the peak of Whistler Mountain, Whistler, British Columbia (hereafter called Whistler Peak). Situated about 100 km from the west coast of Canada, the Whistler Peak site was established to provide a baseline of particles and trace gases in the lower free-troposphere, and to examine incidences of trans-Pacific transport of dust and pollution into western Canada. This paper presents O_3 and CO measurements from 2002-2006, including their annual and interannual variability. Enhancement of CO and O_3 for trans-Pacific air masses is identified for springtime versus summer and compared to the relative enhancement in North American air masses above the Pacific background. The summer enhancements observed in O_3 and CO are then related to the interannual variability of forest fires.

2 Experimental

2.1 Site Details

Whistler Mountain, approximately 100 km north of Vancouver, is part of the Coast Mountain range, a subset of the Pacific Cordillera extending along the west coast of North America from

Alaska to Southern California. This high elevation site (50.06 N, 122.96 W, 2182 m-asl) was chosen because of its relatively high exposure to the background troposphere, low impact expected from local pollution, and year-round accessibility. It is located just above the Whistler glacier, approximately 400 m above the tree line. The mountain peak is usually snow covered except for July to September. Whistler village lies just north of the site at about 650 m-asl elevation. Vegetation in the surrounding valleys is mixed forest, dominated by coniferous trees.

Samplers are located in the chair lift operator's hut. Access is provided through Whistler-Blackcomb mountain operations. The site operates year round although for about one month during each of the late spring and fall, operator-required sampling is suspended because of limited site access. Pollution influences from trucks, snowmobiles or snow grooming equipment are readily identified and have been removed from the dataset.

Trace gases are sampled through a ¼" Teflon sample line, with a 5 µm in-line Teflon filter to remove particles and mounted approximately 5 m above the ground. All site measurements were recorded, and are reported here, as Pacific Standard Time (PST).

2.2 Trace Gases Ozone and CO

Carbon monoxide was measured continuously with a Thermo Environmental Instruments Inc. Model 48C-Trace Level analyzer which determines CO by non-dispersive Infrared Spectrophotometry (NDIR). Calibrations were carried out approximately 3-4 times per year with a NIST traceable standard and were stable throughout the four year period, changing by less than 3%. The accuracy of the calibration points, taken as three standard deviations of the 100 ppbv standard point was within 10 ppbv. The detection level was about 19 ppbv determined as three times the standard deviation of the instrument zero. Instrument zeros were done every two hours for the period of March 2002-2005, every half-hour for March 2005-2006, and hourly after March 2006. The instrument background was taken as a linear interpolation with time between consecutive zeros and this approach was valid when the operating temperature changed monotonically with time. Changes of one-degree of operating temperature could result in a 25 ppbv difference in CO. Installation of a thermostatically controlled fan usually maintained the room temperature to ± 0.5 C. For cases in which the temperature fluctuated within the two-hour

period, the background was calculated as a function of temperature. The standard error on this temperature versus background voltage over a multiple-hour period was 15-20 ppbv.

Ozone was measured with a Thermo Environmental Instruments Inc. UV absorption monitor (TECO 49C). Ozone zeros were carried out every 48 hours with an in-line Koby air purifier cartridge. The instrument was calibrated every 3-4 months with a NIST traceable Dasibi Model 1008 PC ozone calibrator. Over the period March 2002 to March 2006, the calibration factors varied by less than 1%; the detection level was about 0.5 ppbv and the uncertainty of the measured ozone concentrations was within ± 0.5 ppbv.

2.3 Meteorological measurements

Meteorological measurements at the site include temperature, pressure and relative humidity. Pressure is measured with a Vaisala PTB101B pressure sensor. Temperature and relative humidity are both measured with a Campbell Scientific HMP45CF probe. Additional meteorological measurements (wind speed and direction) are made available through Whistler-Blackcomb on an hourly time resolution.

Fog is detected with an optical cloud detector (MCD-05, Associated Weather Services, Inc).

Ten-day back trajectories with the arrival pressure specified at 750 hPa (the approximate mean pressure at the site) were used, calculated with the trajectory model of the Canadian Meteorological Centre (D'Amours and Page, 2001). The model uses 3-D analyzed wind fields and trajectories are calculated on an X by Y grid. Trajectories were calculated for arrival time at Whistler every six hours.

3 Results and Discussion

3.1 Meteorology

Monthly average temperatures from all hours of data at Whistler Peak (Mar 2002 to Dec 2006) range from -8.3 C in winter to 9.4 C in summer. Maximum temperatures are commonly in July and August, although during 2003 the maximum temperature was in June followed by lower-

than–average temperatures during the autumn. The predominant wind direction is westerly to southwesterly with gusts reaching 150 km/h during winter storms.

Clouds also impact this high elevation site. Although the fog detector gives no information on cloud amount, it provides qualitative information on cloud frequency. Data are available for an entire year (Apr 2002 – Jun 2003) and three fall-through-spring periods (Sep 2003 – Mar 2004; Oct 2004 – May 2005; Sep 2005 – Apr 2006). The percent of time during each available period that the site was in cloud at each hour of the day ranged from 8-20% for entirely cloud covered to 15-40% for greater than 10 min out of an hour. Cloud coverage increased from morning to afternoon with a decrease again at approximately 1600 (PST).

Several approaches have been used to separate boundary layer from free troposphere influenced data. Weiss-Penzias et al., (2006) compared water vapour at the Mt. Bachelor site with that from nearby radiosondes. Kleissl et al., (2006), Kleissl et al., (2007) provided a detailed examination of the effects of buoyant upslope flow or mechanical lifting on the Azores Pico site through the use of observed vertical soundings supplemented by those from a European numerical weather model. A simplified approach is used here to estimate the timing of the boundary layer influence on the mountain peak CO and O_3 mixing ratios. In spring 2005 (May) and 2006 (March – June) Whistler Peak temperature data were supplemented by temperature data from the Environment Canada National Archives Climate Database, and additional temperature records from two temporary sensors (MadgeTech, Temp101) to provide temperature measurements at 300 m vertical intervals up the mountain. The calculated temperature lapse rates from 1000 m to 2182 m were compared to the dry and wet adiabatic lapse rates to determine if the air mass was unstable, conditionally unstable, or stable with the assumption that the air mass was mixed under unstable conditions. A value of 1-3 was assigned to each hour based on the stability calculations (1=unstable; 2=conditionally unstable; 3=stable), to estimate of the timing of the transition from stable to unstable conditions. Figure 1 shows the diurnal variation in this "stability index" and in water vapour for the month of May 2006. The calculations confirmed mixing to the site from lower levels during springtime with the transition from stable to conditionally unstable conditions at approximately 800-900 PST and return to stable conditions by 1700-2000 (PST). Although this simple technique only addresses one possible reason for boundary layer influence, it provides some time of day estimates for data segregation, agrees well with a more detailed meteorological

analysis over an entire year (Gallagher et al, 2011), and supports the time of day approach employed by Andrews et al. (2011) for several mountain-top sites. Very little valley influence is expected in winter as the snow covered surface suppresses convective lifting of the boundary layer to the Peak level. Daytime growth of the boundary layer to encompass the mountain site was also confirmed from aircraft profiles of particles and gases during the INTEX-B campaign of spring 2006 (Leaitch et al., 2009). Early morning profiles showed a decoupling of the boundary layer and free troposphere below the peak while the afternoon profiles most often showed a mixed boundary layer up to 3 km.

3.2 Trace Gases

3.2.1 Influence of Boundary Layer or free troposphere

The extent of the boundary layer influence is considered next by examination of the diurnal cycles in O_3, CO, and water vapour as a function of season (Figure 2). (Note that although the absolute values differ among the seasons, the ranges are consistent in all four panels). In winter (Fig 2a) there is little diurnal variation with O_3 changing by less than 0.5 ppbv. Water vapour begins to increase at approximately 1000 PST and CO changes by less than 1 ppbv throughout the daytime. Overnight, CO mixing ratios average 1-3 ppbv higher than daytime values. The reason for this increase is unclear and may be an indication of transport layers. The possibility of increased influence from grooming equipment overnight in winter may be considered but would not explain the repeated pattern in fall. As the valley warms, during the late spring months and early summer (MJJA), the mountain site becomes more influenced by valley air mixed up to the site. In summer (Fig 2b), a decrease in averaged ozone is observed at approximately 0800-0900 PST as the nocturnal inversion in the valley breaks up and air with lower ozone reaches the site. This decrease in ozone is coincident with increases in water vapour and CO, both indicative of the boundary layer influence. At lower elevations in the nocturnal boundary layer, ozone may be lost through titration with NO or also through deposition processes. When mixing begins in the morning, the Peak first sees the effects of nighttime ozone loss but then by mid-day ozone begins to rise as mixing continues and ozone may be mixed down from higher elevations to the Peak. By late afternoon, ozone often exceeds its nighttime value, peaking at approximately 1700-1800 PST. This late afternoon rise to values on average 1 ppbv higher than nighttime may be due to

photochemically-produced ozone and is coincident with a secondary CO peak. CO is not only a good tracer for pollution and biomass burning, it also increases as a result of the oxidation of biogenic NMHCs (e.g. Hudman et al., 2008; Slowik et al., 2010) which may contribute to this secondary peak. In summer, the average maximum diurnal changes in CO and O_3 during JJA are 6 ppbv and is 3.5 ppbv respectively (Fig 2b). The spring (Fig 2c) and fall (Fig 2d) months show similar patterns with the ozone decrease happening later in the morning and with the overall diurnal change reduced; photochemical production is lower than during summer. The largest diurnal variation in ozone was during July 2004 at approximately 10% change about a daily mean value.

To minimize the impact of the boundary layer chemistry on calculating averages for the free troposphere, the monthly mixing ratios are calculated from nighttime data only (2000-0800 Pacific Standard Time). It is noted, however, that 81% of the averages showed differences of less than 1% between all hours and nighttime only; the largest difference in monthly averages calculated with all data and nighttime only data was 2.2% for O_3 (June 2005) and 1.6% for CO during (August 2002, August 2004).

3.2.2 Ozone

Ozone for March 2002 to Dec 2006 at Whistler Peak is given in Fig. 3a as monthly averages of nighttime data with the 5-year average annual cycle superimposed. As also shown in Figure 4a, the ozone mixing ratios mostly range from 20-60 ppbv (90% of data are between 28 and 53 ppbv) with greater variability in spring and summer values. Monthly-averaged ozone varied from a high of about 45-50 ppbv in springtime to a low of 32-40 ppbv in summer. Annual median mixing ratios ranged from 40 to 43 ppbv over the years 2002 to 2006 (Table 2). These are 15-20 ppbv higher than the annual medians (23-27 ppbv) reported at a regional coastal site in British Columbia for 1992-2001 (Saturna Island) but consistent with high elevation sites in the Western United States; annual medians at Lassen National Park, California (1995-2001) were 38-43 ppbv (Vingarzen, 2004). This range of values is also consistent with annual baseline values determined for the Canadian coastal sites (19 ppbv) and US coastal sites (39 ppbv), by Chan and Vet (2010) who acknowledged that site elevation was a major difference between the two groups.

The amplitude of the annual signal (approximately 14 ppbv) is 5 ppbv less than that reported for Cheeka Peak (Weiss-Penzias et al., 2004) or Trinidad Head (TDH), California (Oltmans et al., 2008) which are both lower-altitude marine boundary layer sites. The observed ozone cycle at Whistler differs from other high elevation sites in the western US such as Rocky Mountain and Lassen National Parks (Jaffe and Ray, 2007; Jaffe, 2011) or from ozonesondes flown at TDH (Parrish et al., 2010). These sites have the spring ozone peak but also have a significant summer peak, sometimes exceeding the springtime maxima. The Whistler ozone data do not show this broad summer maximum and more closely resemble the annual ozone pattern from the coastal TDH site (Oltmans et al., 2008) although monthly median mixing ratios are 3-15 ppbv higher at Whistler (O_3 WHI = 0.7 (O_3 TDH) +19.8 ppbv; R^2 = 0.74, n=56). The small secondary peak often observed in August at Whistler was not observed at TDH, and corresponded with increases in Whistler CO, possibly indicative of regional pollution or influences of biomass burning. Seasonal ozone mixing ratios from Mt Bachelor for 2004-2009 reach a maximum in springtime at 50 ppbv for free-troposphere (FT) air masses and 44 ppbv non free troposphere (non-FT) (Ambrose et al., 2011). In fall through spring, the Whistler seasonal averages fall mid-way between the FT and non-FT values reported at Mt Bachelor but in summer, ozone at Whistler agrees most closely with the non-FT value of 39 ppbv.

It is possible that the broad spring-summer maximum is not observed at Whistler because it is influenced more by the boundary layer in summer than are other elevated sites in the Western US. This was explored by comparing ozone mixing ratios from ozonesondes flown from Kelowna, BC, (49.94 N, 119.4 W), a site approximately 300 km east of Whistler (Tarasick and Slater., 2008). Figure 3c shows monthly averaged ozone mixing ratios measured from ozonesondes for the altitude range 700-800 hPa from Nov 2003-Dec 2006. With the exception of April, May and August 2006, data are available from 1-4 sondes per month. Mixing ratios agree well between the two sites and the sonde data also show a decrease in ozone from spring into summer but this decrease is less than that observed at Whistler. The variability in data from these weekly sondes is high but in August 2006, daily sondes were flown late afternoon and the mean O_3 for 700-800 hPa is 8 ppbv higher than at Whistler. Future investigation of vertical profiles through the ozonesonde intensive sampling periods will provide additional insight into the spring-summer differences in ozone mixing ratios.

The highest positive anomalies in ozone in relation to 5-year monthly means (Fig 3a) were in fall 2002 through spring and summer 2003 with ozone up to 10% higher than the 5-year average. Frequency distributions of O_3 over the summer (JJA) period (Fig. 4a) illustrate the shift in O_3 to higher values throughout summer 2003; the mode has shifted from 36 ppbv to about 45 ppbv. The summer 2004 distribution is bimodal with a high mode at 55-60 ppbv and low mode ~ 35-40 ppbv, corresponding to the location of the single modes for 2002, 2005, 2006. This higher shoulder mode in 2004 is related to air masses influenced by biomass burning and is also reflected in the distributions of CO (Fig 4b).

3.2.3 Carbon Monoxide

Monthly averages of nighttime-only carbon monoxide are shown in Fig 3b. On average, CO ranged from 100 to 200 ppbv, exhibiting a strong seasonal cycle with the maximum value in springtime and minimum in summer. There is a higher degree of variability in summer than winter (the standard deviation for winter data is 14-19 ppbv and for Jun-Aug is 16-27 ppbv) resulting from increased regional emission sources during summer and an increase of boundary layer influence. This annual cycle is consistent with other remote sites on the west coast of North America (eg. Cheeka Peak; Weiss-Penzias et al., 2004). CO mixing ratios at Whistler are remarkably similar to those reported for Mt Bachelor for the period spring 2004 to summer 2005 (Reidmiller et al., 2008) although the values at Mt Bachelor are 15-20 ppbv lower than the Whistler values for Oct 2006-July 2007.

The seasonal cycle in CO has been well documented (Novelli et al., 1998; Novelli et al., 2003) and is attributed to a combination of photochemistry and transport. It is characterized by a slow increase in CO throughout the fall and winter followed by a rapid decline in springtime as OH concentrations increase (Novelli et al., 1998). The main sources of CO in the northern hemisphere are combustion of fossil fuels, biomass burning, oxidation of methane and oxidation of non-methane hydrocarbons (NMHCs) whereas the main sinks of CO are oxidation with OH and transport of CO to the southern hemisphere (Novelli et al., 1998; Holloway et al., 2000).

Novelli et al., (1998) show that in the absence of biomass burning, not only are the CO concentrations reduced but also the maximum CO is shifted to earlier in the year to coincide with the OH minimum. At Whistler, the annual maxima occur in February or March except for 2003,

a year with high Asian biomass burning influence (van der Werf et al., 2006), when the maximum was in April. The variation in monthly-averaged CO from year to year is lowest in Feb-Mar (9-12 ppbv) and highest in May (52 ppbv). Highest CO mixing ratios were observed throughout fall 2002 and spring-summer 2003 but did not continue through fall 2003.

Autumn 2002 and spring-summer 2003 were periods of highest CO anomaly at Whistler Peak; mixing ratios averaged 21% higher in Sep-Oct 2002 and 25% in April-Aug 2003 than the corresponding mean values for all five years. Anomalously high CO during these months has been reported from other northern hemisphere sites and is attributed to Siberian biomass burning (BB) during the summers of 2002 and 2003 (Yurganov et al., 2005; Jaffe et al., 2004). The anomalies in Northern Hemisphere boundary layer stations calculated relative to 2001-2002 values were a maximum of 35% in 2002 and 36 % in 2003 compared with total column anomalies of 19% in 2002 and 25% in 2003 (Yurganov et al., 2005). The CO anomaly is not observed through the fall of 2003. The maxima in Siberian biomass burning emissions (van der Werf et al., 2006) were in August of 2002 and in May of 2003. The timing of these BB maxima are consistent with the CO anomalies at Whistler Peak, that is the effect of the late summer 2002 BB maximum was observed through fall 2002 whereas the May 2003 BB maximum strongly influenced the spring.

Fig. 4b shows the frequency distributions of CO during June to August 2002 to 2006. In 2003, the entire distribution is shifted higher by approximately 20-25 ppbv; in other years, the background CO values are generally similar (10^{th} percentiles for June-August are 99, 121, 94, 93, 94 ppbv for 2002-2006 respectively). The 2004 and 2006 spring and summer seasons had two modes at 110 and 130 ppbv for the Jun-Aug period. The summer of 2004 was a high year for biomass burning in Alaska and Yukon Territory (van der Werf et al., 2006) and these fires have been shown to influence pollution levels in eastern North America and across the Atlantic (Pfister et al., 2006; Val Martin et al., 2006; Lapina et al., 2006) A combination of regional fires in British Columbia and the Alaskan and Yukon fires affected the CO mixing ratios seen at Whistler site in June through August 2004. These varying sources are discussed in the following sections.

3.3 Effect of trans-Pacific transport

The influence of various source and transport regions on O_3 and CO measured at Whistler was investigated by segregating the data by 750 hPa air mass back trajectories as calculated by the CMC trajectory model (D'Amours et al., 2001). Boxes were defined to represent different air mass origins and pathways (Fig. 5). CO and O_3 data were averaged over 6-hour periods centered on the arrival time of the air mass. To reduce possible local boundary layer influences and problems with trajectories over mountainous terrain, CO and O_3 associated with trajectories having spent more than 12 of their final 48 hours at altitudes less than 1000 m-asl were eliminated from the analysis. The defined boxes are of different sizes and thus there is an inherent bias in the total amount of time a given trajectory can spend in a particular box. Thus the assignment of a six-hour mean CO or O_3 value to a back trajectory box is based on the residence time of the trajectory above a seasonally varying threshold residence time. For a given trajectory, at least 40% of the total residence time within a box region was determined as the optimal threshold. This threshold maximized the largest number of samples that could be kept for subsequent analyses and minimized the number of trajectories that were attributed to multiple box regions. Mean values of O_3 and CO calculated for threshold values of 20% and 60% of the seasonally varying maximum are also shown for comparison.

Seasonal and interannual differences in the relative transport through the boxes reflect the variations in the synoptic scale climatology controlled by the Aleutian Low and the Pacific High. The composite sea level pressure for DJF (Fig. 6a) and JJA (Fig. 6b) for 2002-2006 illustrate this winter and summer climatology (NCEP Reanalysis data provided by the NOAA/OAR/ESRL PSD, Boulder, Colorado, USA, from their Web site at http://www.cdc.noaa.gov/ (Kalnay et al., 1996). In winter, zonal flow is generally stronger and the Aleutian low results in a southwesterly component of the flow over BC while in summer, the intensifying Pacific High causes a more northwesterly flow over the south coast of British Columbia (Klock and Mullock, 2001). Normalized transport in representative boxes is shown in Fig. 7 along with the 5-year mean CO at Whistler Peak. The frequency of trajectories originating in the Asian box (Box 7) is highest during (Nov-Apr) and lowest during (May-August) reflecting the stronger zonal transport during winter and spring. Transport via the northerly route and passing over Northern British Columbia and Alaska is stronger in spring and early summer (Box 4). In contrast, air masses passing along the west coast of the US (Box 2, not shown) are more often seen during summer. The frequency

of transport to the site from the South part of the North Pacific (Box 8) remains relatively constant throughout the entire year.

Mean values of O_3 and CO for Boxes 7 and 8 are given in Figures 8a and 8b. Box 7 represents air masses with Asian origin and trans-Pacific transport (t-P) and the Box 8 represents the south part of the North Pacific, also defined here as representing the Pacific background. For O_3, differences between Asian-influenced (Box 7) and background (Box 8) air are less than 1.5 ppbv during Nov-Jan and Jul-Aug. The greatest differences are seen in Mar-Jun and Sep-Oct with an average of 6±2 ppbv more O_3 in t-P air masses above the clean background for the entire Mar-Jun period. For CO, mixing ratios in Boxes 7 and 8 are similar during July and August, but for all other months, the CO in t-P air masses ranges from 4 to 25 ppbv more than is seen in the clean Pacific air masses. In Mar-Jun, the mean CO enhancement is 16 ±2 ppbv. The similarities in Boxes 7 and 8 in Jul-Aug may be a reflection of the reduced zonal transport. The CO and O_3 values for Boxes 7 and 8 in Jul and Aug are lower than the mean values for all air masses.

The highest values of CO and O_3 in summer are dominated by local and regional events with transport from the North American boxes, i.e. either up the coast from California or from the north and influenced by Alaska, Yukon or Northern British Columbia. This may be due both to the influence of forest fires or also of urban centers south of Whistler, throughout the Pacific Northwest and northern California. The next section investigates the relative influences of trans-Pacific transport or biomass burning during the spring and summer.

3.4 Effect of North American Boreal Fires

Influence of trans-Pacific transport and of North American sources varies from spring to summer as well as from year to year. Data from May and August are shown as representative of spring transport and biomass burning seasons respectively (Figure 9). The pattern for June is similar to May while the July pattern is similar to August. The O_3 and CO enhancements for trans-Pacific (t-P) (Boxes 6,7) or North American (NA) (Boxes 2, 3, 4, 5) air masses are presented relative to the Pacific background (Box 8) for 2002-2006. The absolute enhancements will depend on the values chosen to represent this background and air masses from Box 8 may be a conservatively high estimate based on the comparison with the 30th percentiles of the data (Table 2). In May,

there is no significant difference between O_3 in t-P or NA air masses in 2002-2005 (i.e. no significant difference and each 0-6 ppbv higher than background (Fig 9a)). In 2006, the t-P air masses averaged approximately 6 ppbv above the background whereas the NA boxes were lower than background by 9 ppbv. Background values may be overestimated for this year resulting in this negative ΔO_3(NA) and a lower background would result also in increased ΔO_3(tP). During the spring 2006 INTEX-B period (Leaitch et al., 2009; Walker et al., 2010) ozone enhancements of about 10 ppbv were estimated in Asian air masses arriving at Whistler. For CO (Fig 9b), with the exception of 2005, values in t-P or NA air masses were 5-14 ppbv higher than the background but this enhancement was not consistently dominated by one sector or the other. In 2002, 2004, and 2005 the North American influence was greater but in 2003 and 2006, CO was higher in t-P influenced air masses.

During the summer biomass burning period (as represented by August), the amount of ozone in the t-P boxes relative to background is in the ±2 ppbv range with the greatest enhancement of 3 ppbv seen in August 2003 (Fig 9c). For the NA boxes, however, the greatest ozone enhancement relative to the background occurred in 2004 at about 13 ppbv, followed by 5-6 ppbv increases in 2003 and 2005. Enhancement of CO in NA air masses is always greater than in t-P air masses (Fig 9d). For August 2004, the corresponding enhancement in CO was 43 ppbv for the North American air masses whereas the trans-Pacific enhancement was only 12 ppbv.

These largest summer increases in O_3 and CO are attributed to the North American boreal fires. Total estimates of area burned (Table 1; Sources: US National Interagency Fire Center; Canadian Interagency Forest Fire Centre) in western North America are also plotted on Fig 9 c-d. Fire influence was low in 2002; the most notable western regional fires were in late spring and early summer in Alberta. Influence from this sector is uncommon at Whistler but elevated levels of CO and O_3 were observed with northeasterly flow in mid-June 2002. As noted previously, 2003 was a high year of boreal fires in Siberia which resulted in increased O_3 and CO at Whistler. However, because the entire CO distribution was shifted higher in 2003, the incremental differences in average NA CO above the defined background mixing ratios (Table 2) were not as great as those in 2004-2005. The most notable North American forest fires over these latter years were those in Alaska (AK) and Yukon Territory (YT) in summer of 2004 and in AK in 2005. The 2004 AK and YT fires were the largest on record in terms of area burned (Global fire

Monitoring Centre; http://www.fire.uni-freiburg.de/) and they influenced much of Eastern North America (Pfister et al., 2006) and across the Atlantic (Honrath et al. 2006; Val Martin et al., 2006). In summer 2005, the total area burned in British Columbia was only about 50% of the 10-year average but it was once again another very active burning season in Alaska; the estimated area burned reached almost 70% of the 2004 season. In 2006, fire plumes from California and the US Northern Rockies were both observed at Whistler.

The August enhancement in both CO and O_3 for North American air masses relative to the background, co-varies with the total area burned (Fig 9c-d; see solid circles and red line). For several sites in western North America, Jaffe et al. (2008) have shown an increase in summer mean ozone (1998-2004) with area burned in a 10x10 degree region around each measurement site. This relationship is also evident for the Whistler site and relates increases in ozone to CO, a tracer for combustion. Boreal fires, in addition to their significance in controlling the CO budget, are substantial sources of NOx and NMHCs (Wotawa et al., 2001) and thus additional precursors for ozone formation. These emissions have been shown to have an effect on regional ozone concentrations (Jaffe et al., 2004; Val Martin et al., 2006; Honrath et al., 2004; DeBell et al., 2004; Bertschi and Jaffe, 2005). Pfister et al., (2006) estimated the ozone production from Alaskan and Northern Canadian wildfires during summer 2004 to increase the ozone burden from the surface to 300 hPa (50-70 N, 180E – 60W) by approximately 7-9%. The ozone increase at Whistler for August 2004, is about 35-40% over the background. This analysis does not separate any NA anthropogenic influences from forest fire sources, nor does it consider any changes in North American anthropogenic emissions from year to year.

3.5 Relationship between Ozone and CO

The relationship between O_3 and CO has been examined at various background sites to estimate the degree of photochemical ozone production in the atmosphere (e.g Parrish et al., 1993; Parrish et al., 1998). The close covariance of O_3 and CO at Whistler is shown in Fig 3c with the springtime maxima in CO sometimes preceding that for O_3. For several North Atlantic sites (Parrish et al., 1998) O_3 and CO were positively correlated in summer with O_3 versus CO slopes of approximately 0.3-0.4. Honrath et al. (2004) analyzed 2001 and 2003 O_3 and CO from the

high altitude Azores site (Pico) and found slopes often closer to unity, in part attributed to longer transport times from North American source regions to the Azores. On the west coast of NA, Weiss-Penzias et al., (2004) found slopes of about 0.2-0.3 for O_3 to CO relationship in summer 2001. At Whistler, the slopes of the hourly O_3 to CO relationship as a function of month are shown in Figure 10. The seasonality of the slopes introduced by Parrish et al., 1998 is also seen at Whistler, with positive slopes in spring and summer and negative slopes in winter. Summertime (JJA) slopes of O_3 to CO at Whistler range from a low of 0.21 in Aug 2005 to 0.62 in July 2005 (average slope JJA, 2002-2006 = 0.45). The reduction in slope from July to Aug 2005 is primarily driven by the mixed influence from CO produced by regional and local forest fires in Aug 2005 and their impact at the site. The correlations between O_3 and CO at Whistler (R^2 in JJA of 0.1 to 0.6), however, are lower than those found by Parrish et al., (1998) (R^2 of 0.5 to 0.7) and closer to those observed at Cheeka Peak (maximum $R^2 \sim 0.4$, Weiss-Penzias et al., 2004). This greater degree of scatter between O_3 and CO in the Whistler measurements may be due to the proximity of regional boreal fires and the variation in the chemical processing time of the measured air masses.

The enhancement ratios of O_3 and CO above background values over specific periods also describe the regional O_3 production relative to precursor emissions. The ratios will depend on the values chosen to represent the background. Honrath et al., (2004) used the low modes of the CO and O_3 distributions; Pfister et al., (2008) chose average values of a non-fire impacted air masses; Val Martin et al., (2008) used the 20th percentile of all data for each season and year. The enhancement of O_3 relative to CO in NA air masses is shown in Fig 11 where the background air masses for each month are defined here as the O_3 and CO mixing ratios in (a) Box 8, and (b) the 30th percentile of all data (Table 2). Although there is scatter, Fig 11 shows largest enhancement of O_3 and CO in August relative to May. For months when ΔCO was greater than 10 ppbv, ratios of ΔO_3 to ΔCO range from about 0.2 to 0.6 with the median value of 0.31. The lowest ratio was in June 2004 when the site was influenced by a regional fire. This enhancement ratio is in the range of that calculated in Pfister et al. (2006), of approximately 0.26 ppbv/ppbv downwind of the 2004 fires. Mauzerall et al. (1998) reported different ΔO_3 / ΔCO ratios depending on the age of the air mass ranging from 0.15 to 0.74 for fresh to aged plumes during the TRACE-A experiment. While CO is emitted from fires, O_3 is produced from the fire-emitted precursors as

the air mass moves downstream. Pfister et al. (2008) found that the areas of maximum O_3 and CO are not necessarily co-located. The relationship between O_3 and CO varied and depended on the location of the fire source area relative to Whistler. Selected events observed at Whistler in summer 2005, 2006 are shown in Fig 12 to illustrate the variability in the O_3 to CO relationship at Whistler. For all of these events, the rise in CO was greater than 20 ppbv above background values. Source regions are identified based on back trajectories and satellite analyses NOAA Hazard Mapping System Fire Analysis (http://www.ospd.noaa.gov/ml/land/hms.html). For these examples, fire source areas were southern British Columbia, northern Washington State, Alaska, Yukon and California.

During Aug 9-12 (Fig 12a), CO and O_3 are anti correlated with a slope of -0.14 (R^2 = 0.66); for August 14-17 (not shown), the period of maximum CO (440 ppbv), there is a slight positive slope (0.07) although the correlation is weak (R^2=0.19). Figure 12 also shows 750 hPa back trajectories superimposed on analyzed smoke fields from the NOAA Hazard Mapping System Fire Analysis. In the Aug 9-12 period, the site still appears to be in smoke. For the next period (Aug 24 0300 – Aug 27 2000), the air mass was coming from Alaska but the area directly over Whistler appears free of smoke (Fig 12b). In this period, O_3 and CO were positively correlated (slope of 0.29, R^2 = 0.53).

The final example (Fig 12c) is from the end of the 2006 fire season. For this case, (Sep 1-6, 2006), the source of this fire was southwestern US. Over Sep 1-6 period, CO rose from a baseline value of ~ 110 ppbv to peak at 248 ppbv on Sep 4. Ozone peaked at 65 ppbv, approximately 35 ppbv above the baseline level of 30 ppbv. The calculated O_3 to CO ratio for this episode is 0.25.

Although these examples (Figure 12) are just a subset of the fire events influencing the Whistler high elevation site, they illustrate the diversity in the CO to O_3 relationship with an anti-correlation between O_3 and CO in fresh plumes (or plumes with a major source close to the sampling site); slight positive correlations in plumes accompanied by smoke but with estimated travel times of 1-2 days from the source, and positive slopes of approximately 0.25 to 0.3 ppbv/ppbv for the plumes estimated with travel times of 3-5 days.

4 Summary

Year-round measurements of CO and O_3 from the Whistler high elevation site from 2002 to 2006 provide lower free tropospheric mixing ratios on Canada's west coast. CO exhibits a seasonal cycle with a spring maximum and summer minimum similar to other background sites throughout the northern hemisphere. O_3 exhibits a similar annual variation with an overall pattern like that at the clean marine boundary layer sites on the west coast such as Trinidad Head and Cheeka Peak. It differs from several inland US high elevation sites and also from the 2 km ozonesonde mixing ratios from Trinidad Head all of which exhibit a broad spring-summer maximum. The overall pattern is comparable to ozonesonde data taken from Kelowna, a location 300 km to the east of Whistler although mean summer mixing ratios were 6-7 ppbv lower than the Kelowna data. O_3 mixing ratios were higher at Whistler than at the marine boundary layer sites by 3-15 ppbv throughout the year. The absence of the summer shoulder of ozone at Whistler could possibly be attributed to boundary layer influences or may also be the absence of regional pollution which may play a more dominant role at other elevated sites. A boundary layer influence is observed at Whistler during warmer months throughout the daytime hours. The maximum diurnal cycle for O_3 is in JJA and found to be 3.5 ppbv about a daily mean.

Highest monthly-averaged CO was found in fall 2002 and spring 2003, coincident with increased CO found throughout the northern hemisphere as a result of elevated burning in Siberia. Overall values were approximately 20-25 ppbv higher in 2003, values about 25% above the five year mean.

The influence of different transport and source regions on measured values was examined through a back trajectory analysis. Largest differences in CO and O_3 for air masses originating in Asia relative to the south part of the north Pacific were in fall through spring. The mean enhancements in CO and O_3 for Mar-June were 11 ppbv and 4 ppbv respectively. During summer, very little difference was observed between trans-Pacific air masses and the clean background and highest CO and O_3 mixing ratios were found for air masses originating in North America. During the May transport season, the relative importance of North American or trans-Pacific contributions to increased CO and O_3 varied from year to year. In August, enhancements

in CO and O_3 in North American air masses were generally greater than in trans-Pacific air masses. The greatest effects were observed in 2004 and 2005 for both CO and O_3. This corresponded to higher estimates of forest fires throughout the western US and Canada.

Monthly correlations of O_3 with CO for 2002-2006 were positive in summer and negative in winter. In summertime, these slopes range from 0.21 to 0.62 with the lowest slope in 2005. Correlation coefficients were lower than those reported by Parrish et al., 1998 presumably because of the varying influence of regional forest fires and natural sources during summers at Whistler. The enhancement in O_3 relative to CO was estimated for May – September by calculating the average CO and O_3 above monthly background levels. For months when ΔCO exceeded 10 ppbv, the enhancement ratios ranged from about 0.2 to 0.6 ppbv/ppbv. Relationships between O_3 and CO from individual summer periods from 2003-2006, all influenced by biomass burning, showed a range of slopes from less than zero to 0.4.

The data show the importance of North American biomass burning on both the CO and O_3 mixing ratios measured at this lower free-troposphere site. Although trans-Pacific transport plays a role during winter through spring, it is biomass burning that appears most important during summer in contributing to periods of elevated ozone above the hemispheric baseline. This important source needs to be carefully considered in the development and evaluation of ozone mitigation strategies for Canada's west coast.

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Table 1. Estimates of area burned in western North America and for the Russian Federation for 2002-2006. (Sources: US National Interagency Fire Center; Canadian Interagency Forest Fire Centre; Goldammer et al., 2007)

	British Columbia	Yukon Territory	North West Territories	Alberta	Alaska	US Northwest[1]	US Northern Rockies[2]	Russian Federation
	Ha	Ha	Ha	Ha	Ha	Ha	Ha	MHa
2002	8 586	35 669	27 089	496 515	880 865	446 648	153 909	10.6
2003	264 736	48 785	127 821	74 874	226 354	145 973	479 700	17.9
2004	220 516	1 720 324	515 621	236 090	2 689 528	49 629	27 035	4.4
2005	34 664	170 694	218 133	60 763	1 796 862	138 030	232 197	9.3
2006	139 201	95 034	53 398	118 762	107 754	386 851	920 240	13.1

1. Northwest is Oregon and Washington; 2. US Northern Rockies is the sum of Idaho, Montana, North Dakota, and Wyoming.

Table 2. Monthly background values defined for CO and O_3 as average mixing ratios from Box 8. The 30th percentiles of all data are also shown in parentheses.

	O_3					CO				
	2002	2003	2004	2005	2006	2002	2003	2004	2005	2006
May	43 (42)	48 (46)	45 (44)	44 (42)	48 (43)	146 (140)	184 (179)	150 (148)	142 (132)	142 (149)
June	39 (38)	43 (39)	40 (37)	36 (34)	40 (38)	124 (123)	156 (153)	130 (125)	109 (112)	114 (123)
July	37 (32)	38 (33)	36 (33)	29 (29)	34 (29)	118 (102)	132 (126)	109 (106)	90 (93)	100 (94)
August	37 (31)	38 (37)	35 (30)	37 (33)	38 (34)	118 (104)	134 (132)	97 (95)	117 (109)	104 (107)
Annual Mean (Median)	41 (41)	43 (43)	41 (42)	41 (40)	42 (41)	153 (151)	160 (160)	141 (143)	138 (138)	135 (137)

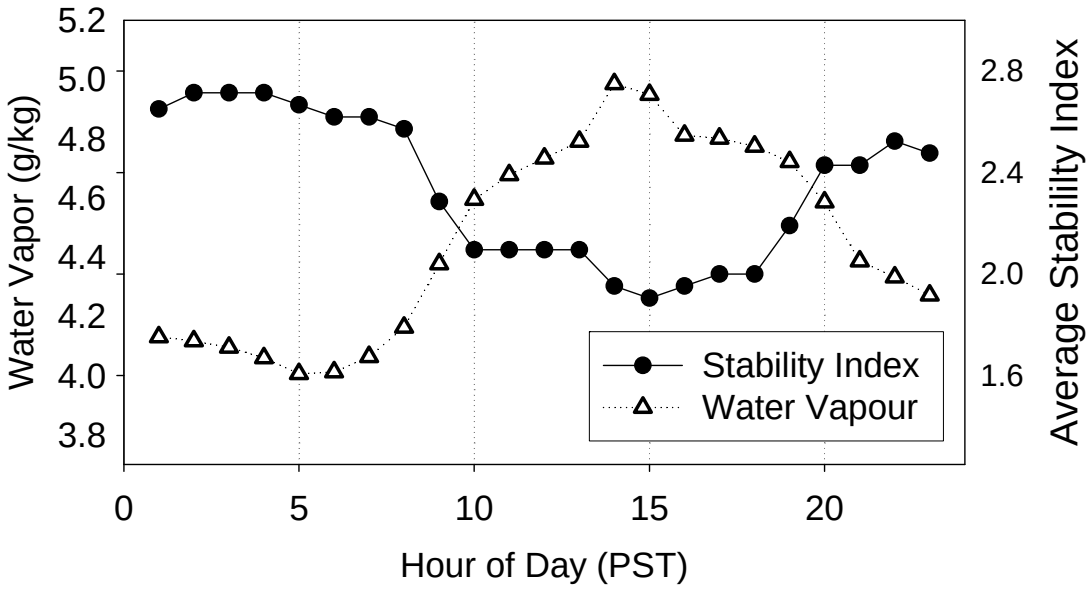

Figure 1: Diurnal variation in water vapour and stability at Whistler Peak for May 2006. The stability Index of 3 describes stable conditions and 1 is unstable or assumed mixed conditions.

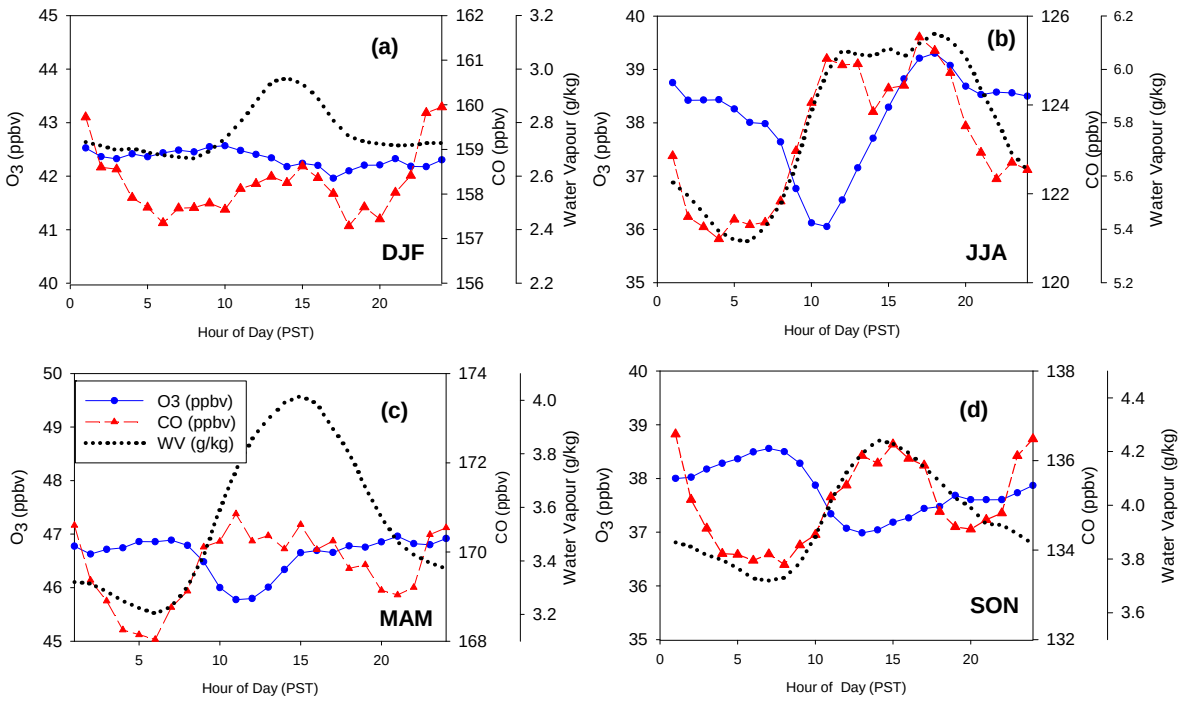

Figure 2: Diurnal variation in ozone, CO, and water vapour at Whistler Peak 2002-2006 for (a) December-February, (b) June-August, (c) March-May, and (d) September-November. CO diurnal variations have been calculated from hourly data smoothed with a three-hour running average.

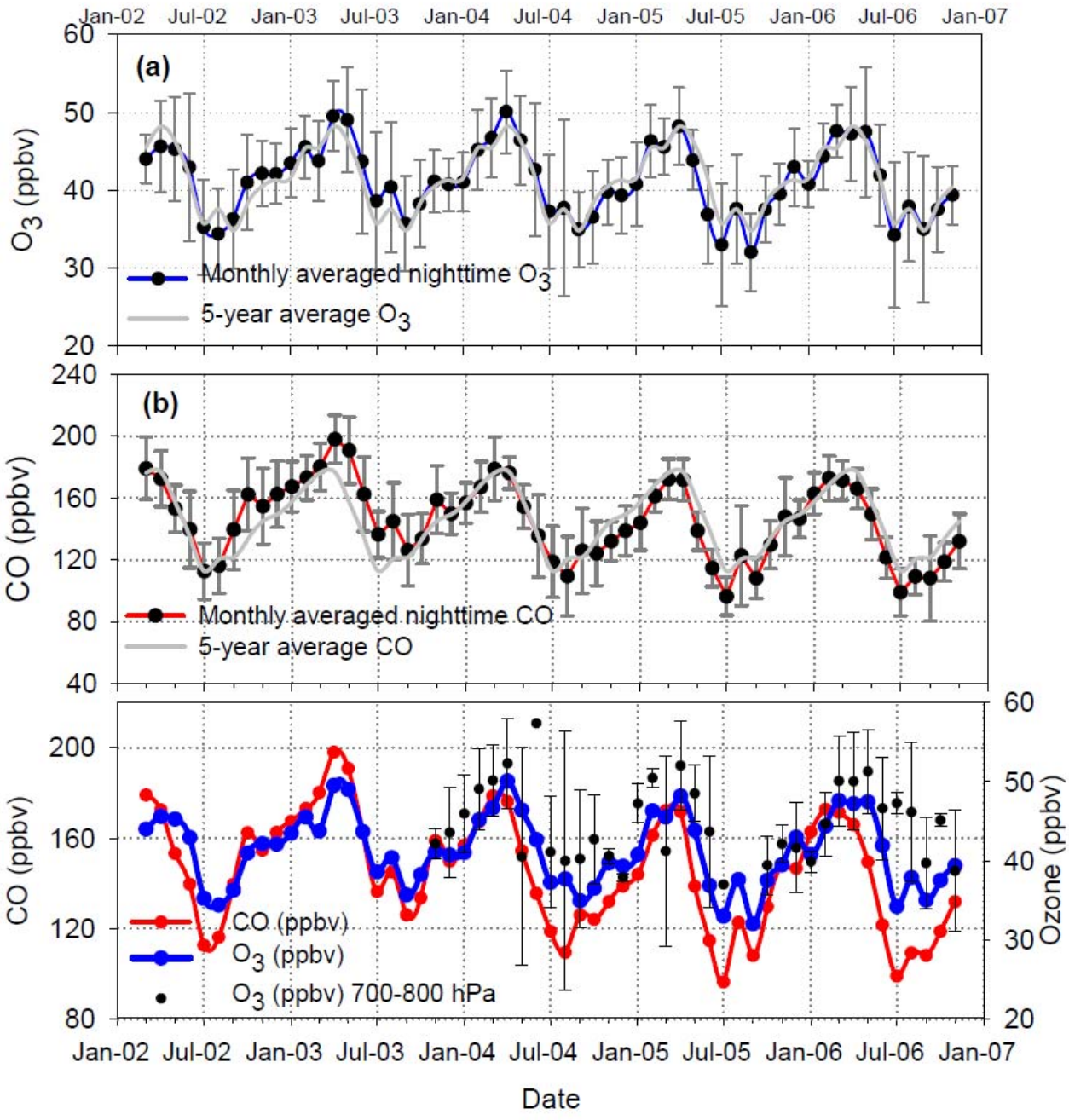

Figure 3: Monthly averages of (a) O_3 and (b) CO nighttime data (1800 – 0800 PST) for Mar 2002 to Dec 2006 at Whistler Peak. Error bars are one standard deviation about the mean of all hourly data. The gray lines show the 5-year averages. (c) Monthly averages of both O_3 and CO from Whistler peak and O3 mixing ratios from ozonesondes flown at Kelowna, British Columbia. The error bars are one standard deviation of the reported values of O_3 from 700-800 hPa.

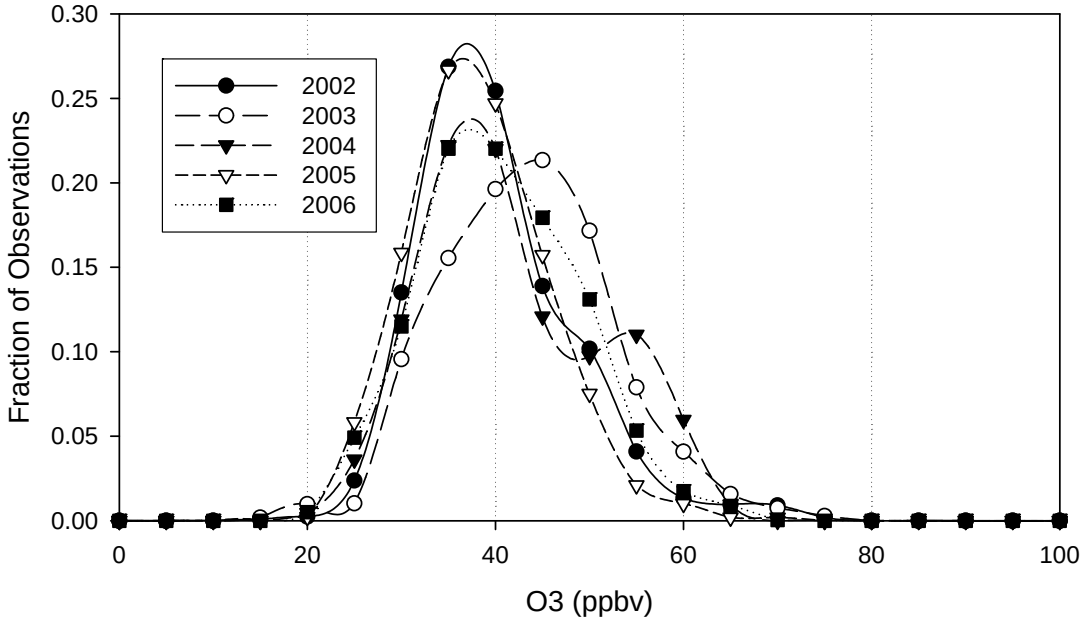

Figure 4a: Frequency distributions of O_3 mixing ratios for June-August 2002-2006.

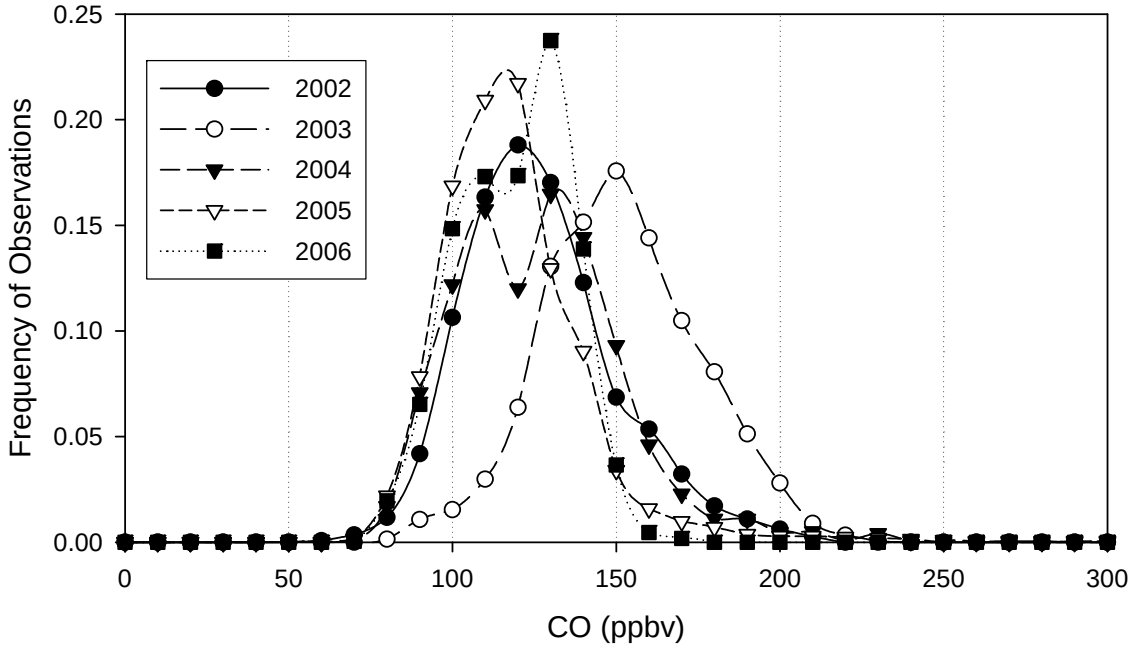

Figure 4b: Frequency distribution of CO mixing ratios for June to August 2002-2006.

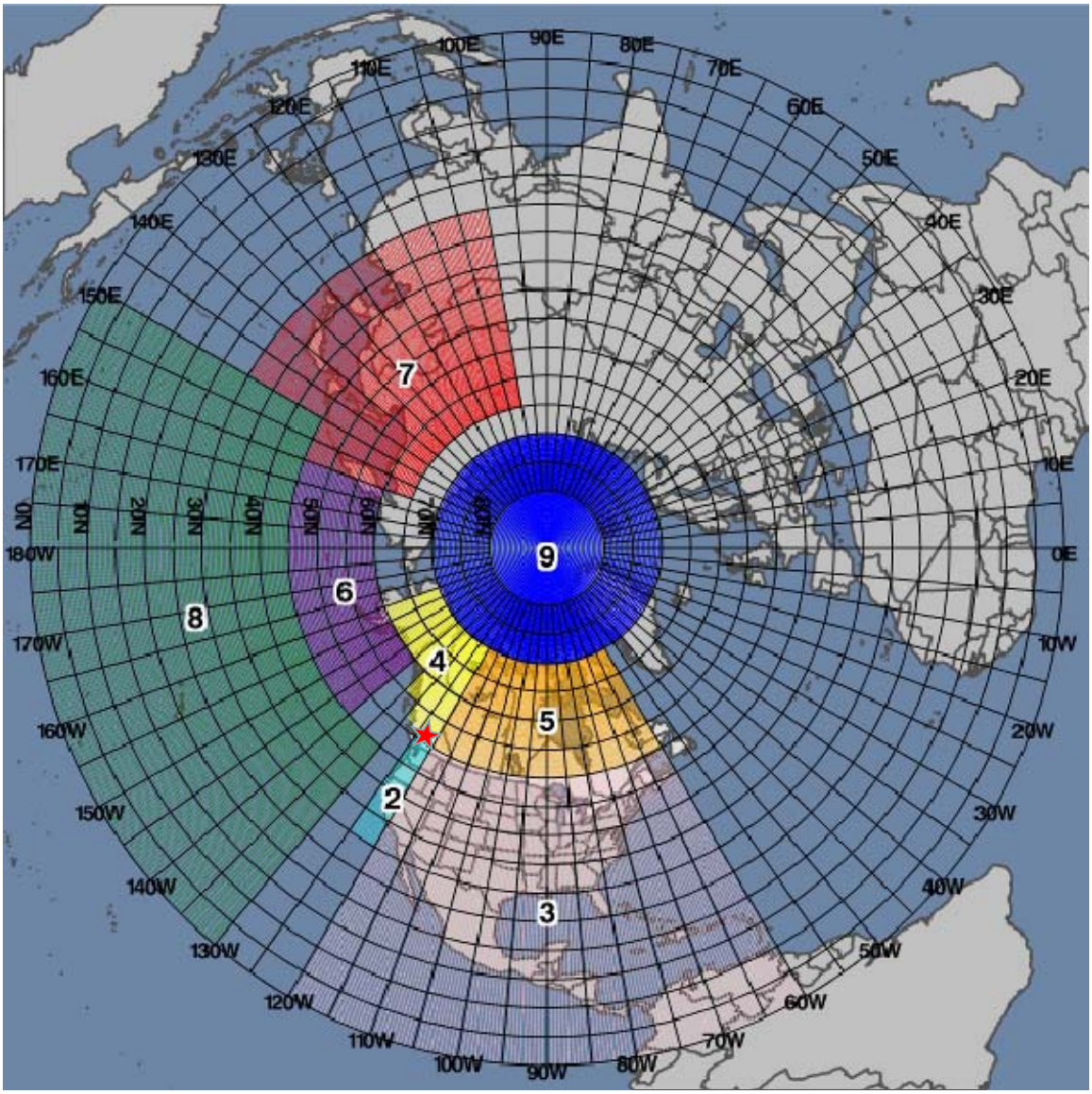

Figure 5: Locations of boxes defined for trajectory analysis. Boxes 2-5 represent North American influence; Boxes 6-7 represent Asian sources and trans-Pacific transport; Box 8 is the southern part of the North Pacific.

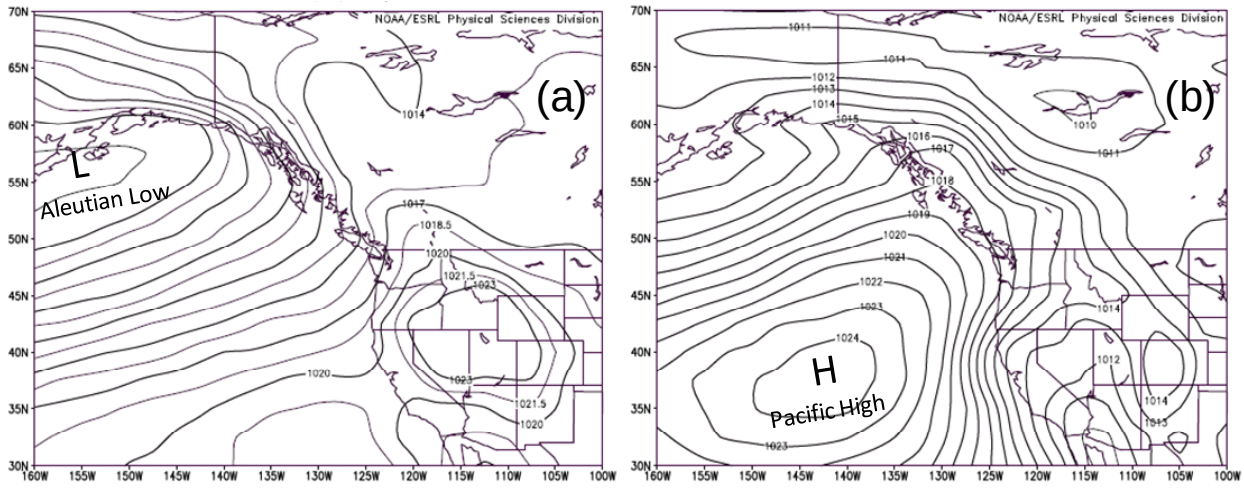

Figure 6: Composite mean sea level pressure from NCEP/NCAR (*http://www.cdc.noaa.gov*) reanalysis for (a) Dec-Feb 2002-2006 and (b) June-August 2002-2006.

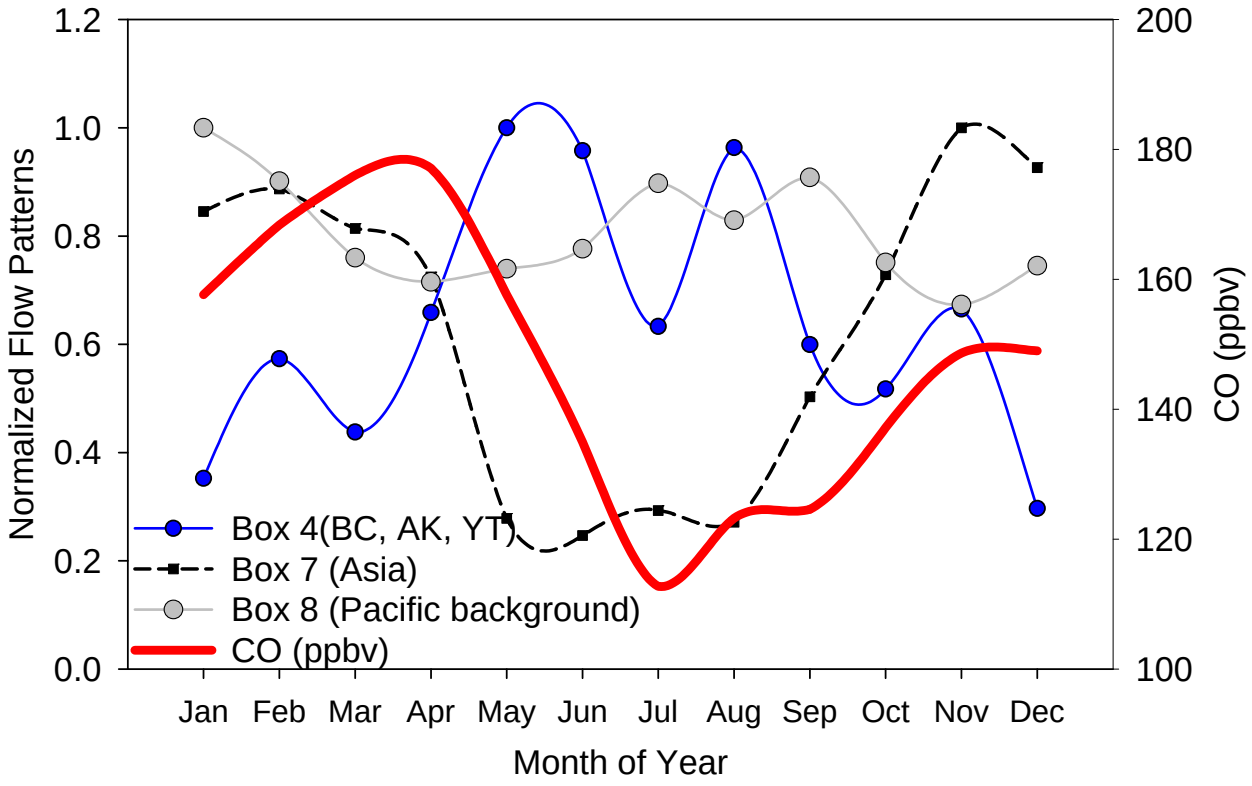

Figure 7: Normalized frequency of transport through boxes defined in Fig 5 as a function of month of year. Box 4 is British Columbia, Alaska, and Yukon Territory; Box 7 is Asia; Box 8 is the southern part of the north Pacific.

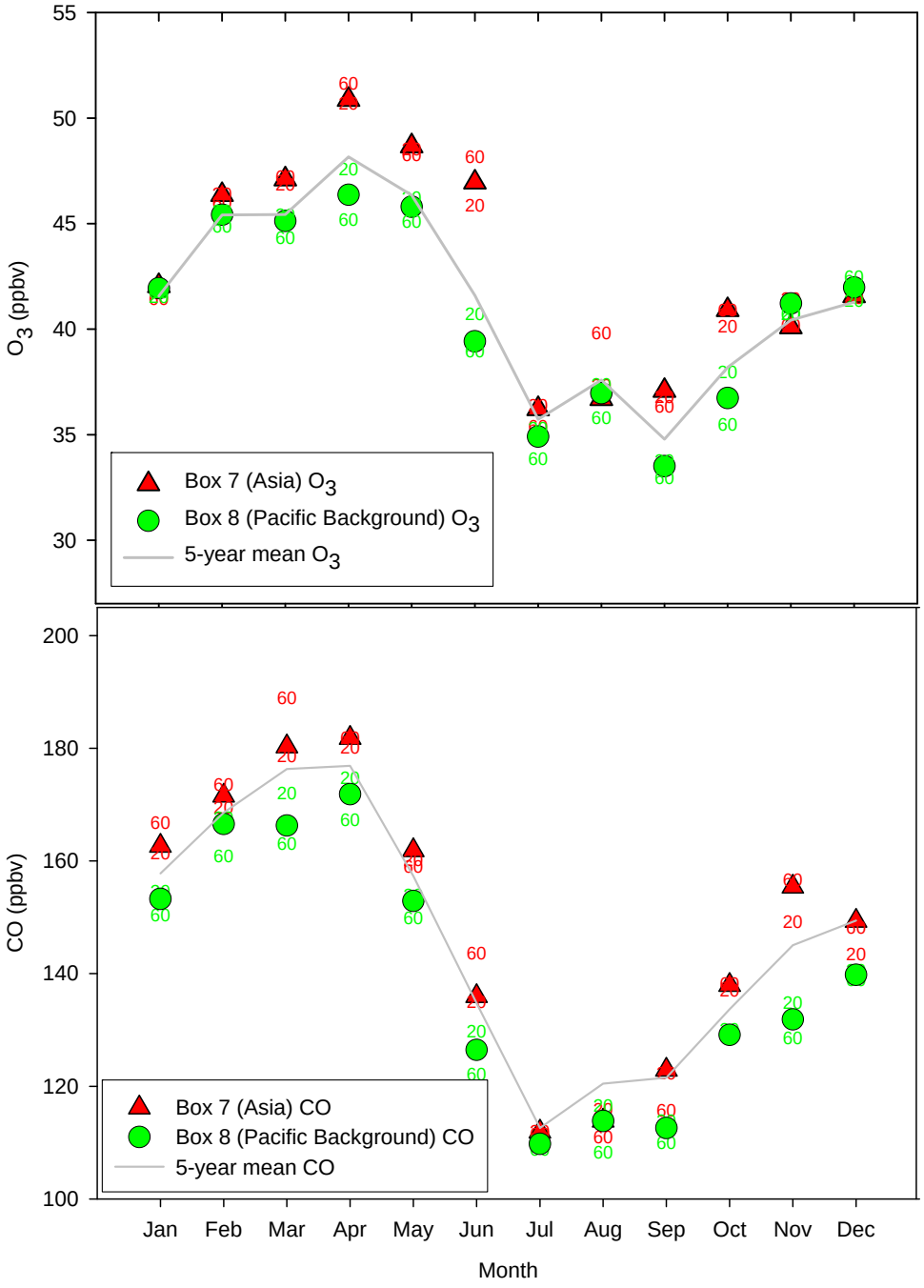

Figure 8: (a) Mean values of O_3 associated with transport through Boxes 7 and 8 as a function of month of year. Boxes are assigned based on 40% of the seasonally varying maximum time in a box. For comparison, mean values for 20% and 60% of time in a box are also shown. (b) As in (a) but for CO.

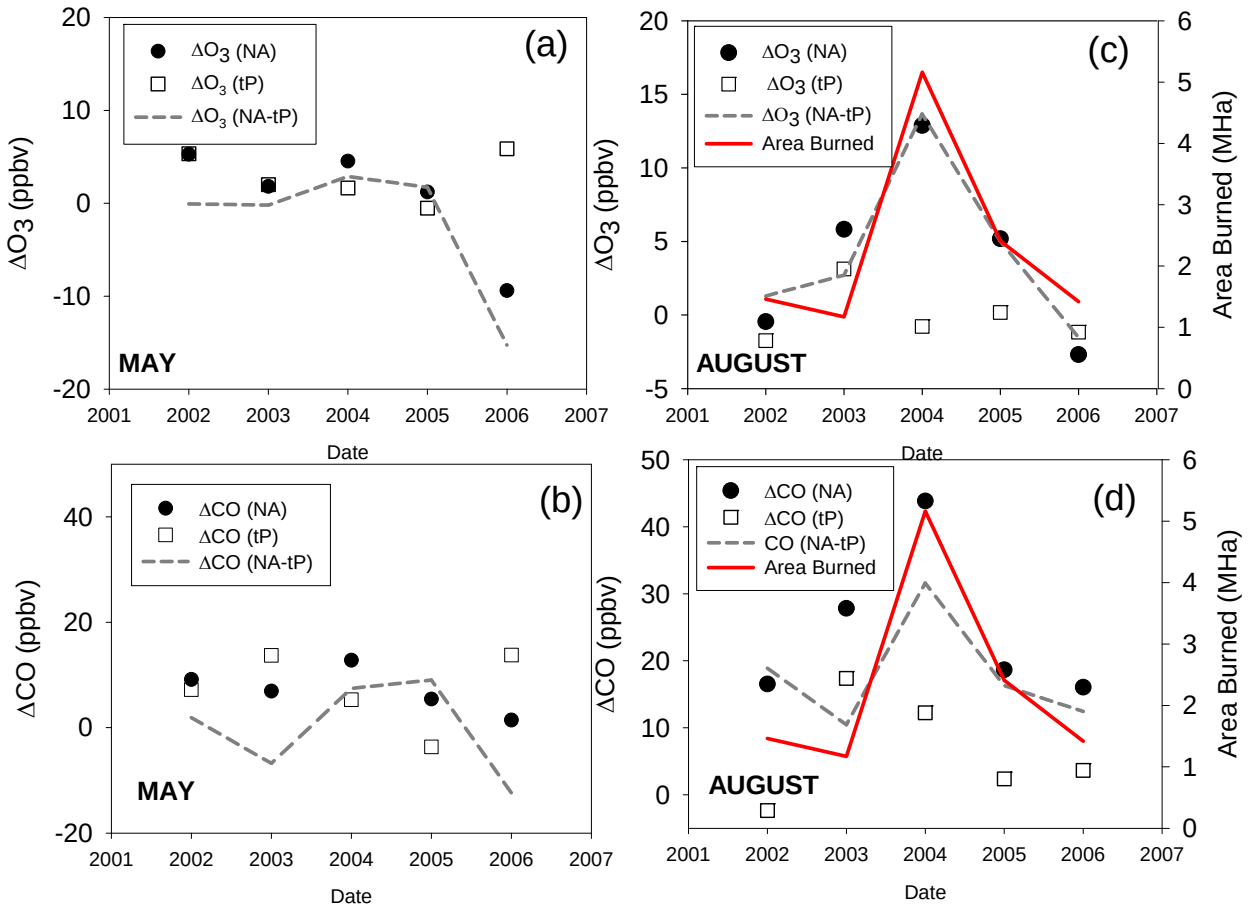

Figure 9: (a) Mean O_3 mixing ratios in North American and in trans-Pacific boxes minus the clean Pacific background in May 2002-2006. The dashed line shows the difference between NA and t-P O_3; (b) as in Fig 9a but for CO; (c) as in Fig 9a but shows ΔO_3 for August; (d) as in Fig 9c but shows ΔCO for August. The red line shows the sum of western North America area burned as reported in Table 2.

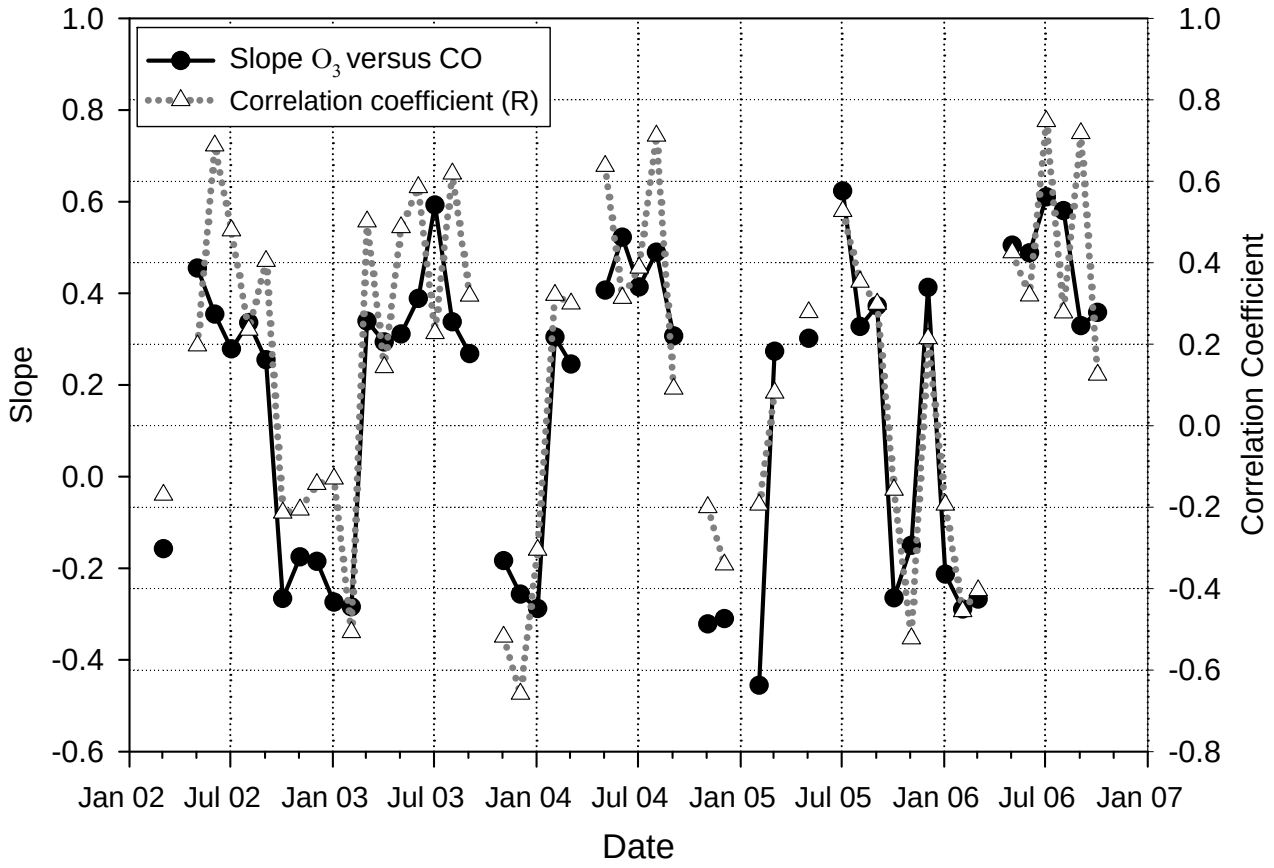

Figure 10: Time series of slope and coefficient of determination for hourly O_3 versus CO relationships for each month based on the reduced major axis regression. The slopes are not shown when the p-value of the regression is less than 0.05.

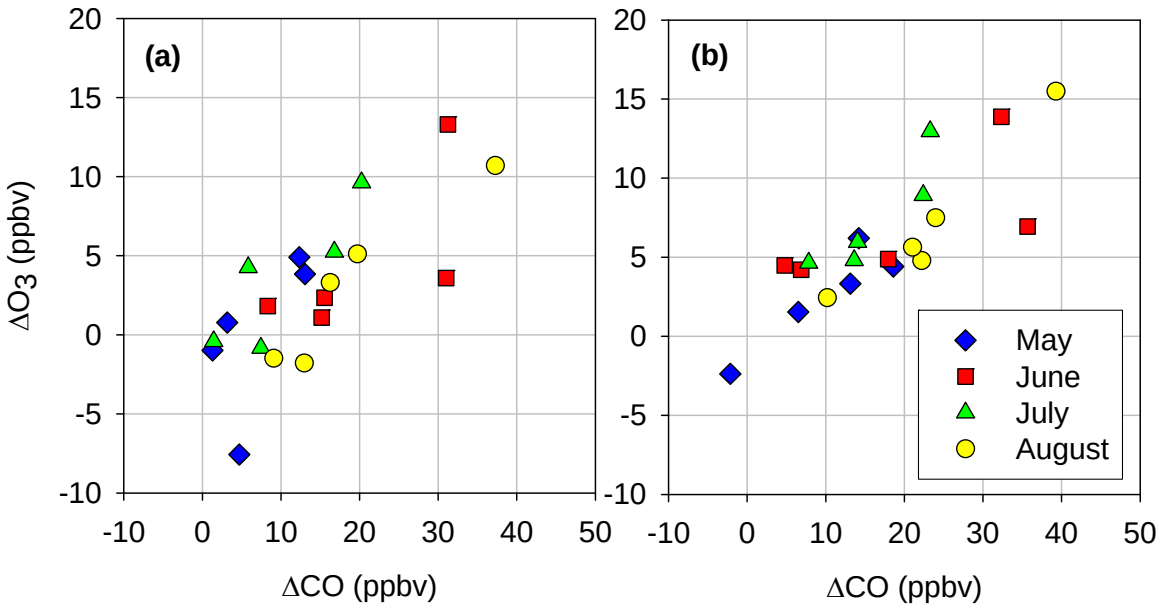

Figure 11: Scatter plot of ΔO_3 vs ΔCO on a monthly basis for 2002-2006 where ΔO_3 and ΔCO are the differences between the North American averages and the background values defined as the average from (a) Box 8 and (b) the 30th percentile of all data for each month.

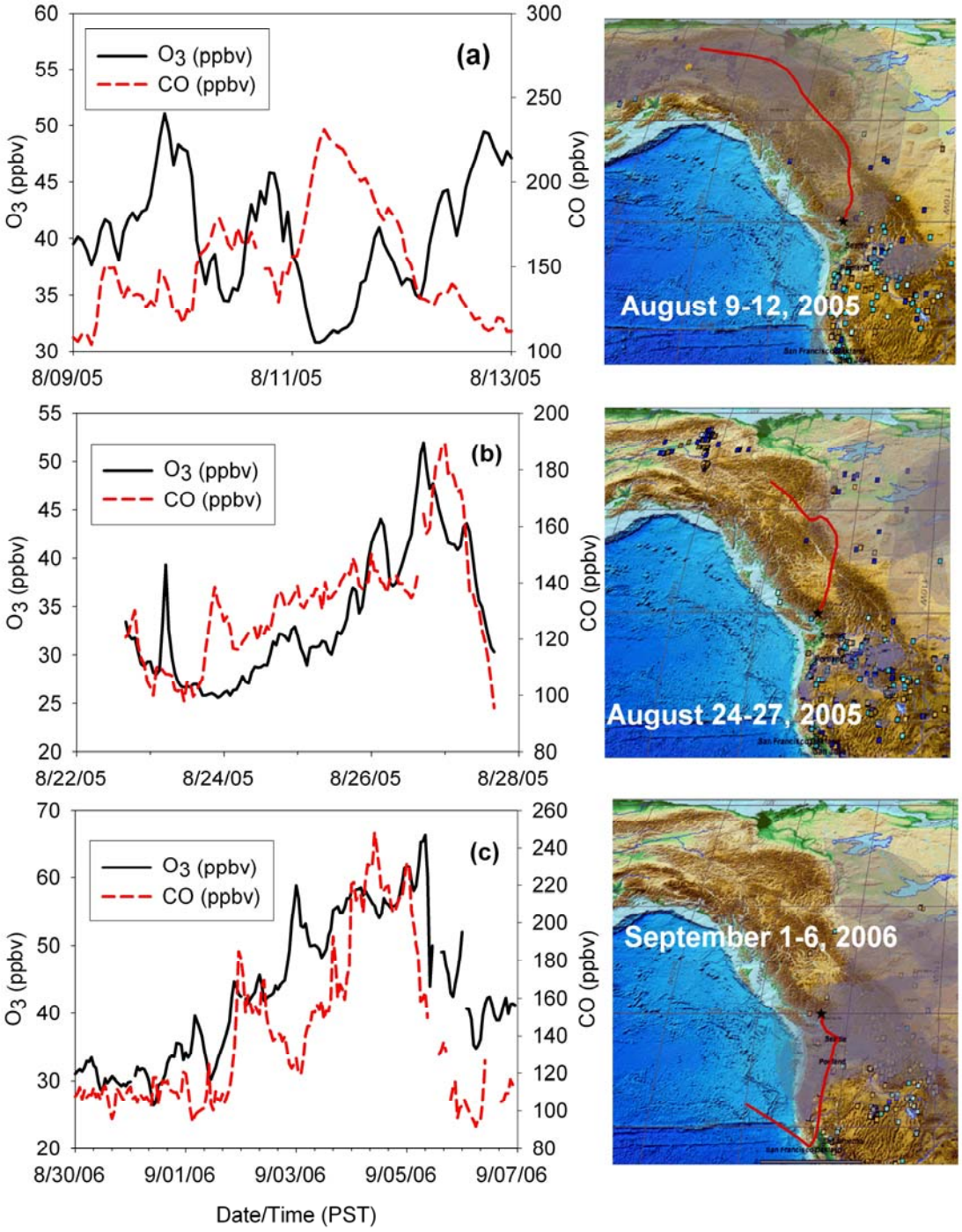

Figure 12: Time series of O_3 and CO mixing ratios and analyzed smoke from the NOAA emission viewer for (a) August 9-13, 2005; (b) August 24-27, 2005; (c) Aug 31- Sep 6, 2006. The panels on the right show analyzed 750 hPa back trajectories from Whistler superimposed on

analyzed smoke fields provided through the NOAA Hazard Mapping System Fire Analysis (http://www.ospd.noaa.gov/ml/land/hms.html).

Figure Captions

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