Atmos. Chem. Phys. Discuss., 11, C10549–C10563, 2011
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Atmospheric Chemistry and Physics Discussions

Interactive comment on "Interannual variability of ozone and carbon monoxide at the Whistler high elevation site: 2002–2006" *by* A. M. Macdonald et al.

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Received and published: 18 October 2011

We thank both the anonymous reviewer and Dave Parrish for reading this manuscript and providing valuable comments. We believe that their concerns have been addressed and that the manuscript has been improved. Changes to the manuscrips are highlighted in the attached supplement.

Reviewer 1 comments

Line 25, page 17624 – line 7, page 17625: the NASA Tropospheric Chemistry Program (formerly GTE) has been reporting on the impact of regional to global transport on the chemical composition in the free troposphere since the early 1980s. In recent

years much research has been conducted to understand such impact using satellite retrievals. This review paragraph needs to be expanded and updated.

Author Response: The paragraph has been expanded and updated to include references to aircraft studies from the NASA TCP and also to include references to satellite retrievals.

“Major field campaigns over the Pacific since the early 1980s have provided coupled CO and O3 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).”

Line 27, page 17629 – line 2, page 17630: The decrease seemed to be over 08 – 10 PST in Figure 3a. The authors might want to be specific about the source(s) of lower O3 levels which decreased the nighttime mixing ratios at the site. After 10 PST what process(es) possibly contributed to the increase besides that 1 ppbv due to photochemical production?

Author Response: Figure 3 (now called Figure 2) has been changed to separate the diurnal patterns in O3, CO and water vapour by season. In summer, the decrease in ozone begins between 08-09 PST but does continue until approximately 11 PST. This decrease in ozone is coincident with the increase in water vapour and an indication of transport of boundary layer air to the peak site. Throughout the night in the boundary layer, ozone may be lost through titration with NO and also through deposition processes. When mixing begins in morning, the Peak first sees the effects of nighttime ozone loss but then as mixing continues, ozone-rich air from higher altitudes may be brought to the Peak level. These points are included in the text.

Line 7, page 17630: The fall pattern looks different from the spring and summer ones based on what Fig. 3a shows. In the fall months nighttime O3 mixing ratios appeared

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to be higher than the daytime levels by _ 1 ppbv with the daily maximum at around 07 PST. Please explain what might have contributed to that.

Author Response: The amplitude of the fall pattern is less than that of summer and the timing of the morning ozone decrease is later because of the later heating and start of vertical mixing. In SON, the increase in ozone from 37.9 at midnight to 38.6 at 07 PST corresponds to a decrease in pressure at the site and most likely represents more influence from subsiding air masses. What is more difficult to explain is the repeatable enhancement in CO overnight during fall through spring. This influence is not apparent in summer. We have investigated the possibility of influence from grooming equipment overnight but not only have the immediate plumes been removed, but there is very little grooming on the mountain during SON. It may be CO in a transition layer between the boundary layer and the cleaner air aloft although we cannot assign a source to this.

Lines 1-2, page 17631: In Table 2, the "summer" values ranged over 29 – 43 ppbv, not 32-40 ppbv as the authors stated, assuming the summer the authors defined includes JJA, and the annual median ranged over 41 – 43 ppbv, not 40 – 43 ppbv.

Author Response: The reference to Table 2 is incorrect because it presents the background values and not the summer mean values. This has been corrected. The annual median does range from 40-43 ppbv.

Line 25, page 17631: I wouldn't call what is shown in Figure 5a "histograms".

Author Response: We have changed this to frequency distributions.

Lines 2-3, page 17633: Relative to what are mixing ratios in September-October 2002 and April-August 2003 "21%" and "25%" higher, respectively?

Author Response: This mixing ratio anomalies as reported are relative to the mean of all five years. This has been clarified in the text.

Lines 24-28, page 17638: The authors might want to consider comparing their slope values quantitatively with recent studies on O3-CO correlation in fire plumes. I recall

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Parrish et al. (1998) did the work for the North Atlantic region, and they were discussing the O3-CO relationship in the North American outflow. What numbers did they get? Please be quantitative. But why would the authors compare their numbers with that study in the context of fire influence?

Author Response: The slopes for the O3 to CO relationship for various sites are reported in the text. In Lines 24-28, we discuss the correlation coefficients of the monthly O3 and CO relationships. For the summer (JJA) correlations reported in Parrish et al., 1998, the square of the correlation coefficients ranged from 0.5 to 0.7. For the Whistler site, the R2 values for JJA over 5 years range from approximately 0.1 to 0.6. The comparison with the sites on the east coast of North America is to illustrate the increase in scatter at Whistler which we attribute to the often-seen fire influence at Whistler in the 2002-2006 data set.

Line 9, page 17640: Were O3 and CO really negatively correlated? There seemed to be a phase lag between the O3 and CO spikes. I saw the CO peak led by about two days. What if the authors correlated the two gases with that phase lag accounted for? I suspect it'd be a positive correlation. Thus, I think here one needs to point out that in some cases there were not phase lags in occurrence of O3 and CO enhancements due to fires, while other times there were such phase lags; it'd be edifying to find out what may have contributed to that.

Author Response: The intention of this part of the discussion is to explain some of the increase in scatter in the CO and O3 relationship, to illustrate that forest fires often play a role in the CO and O3 as measured at Whistler in summer, and to illustrate that in the fire plumes, CO and O3 are not always correlated. In Fig 13a, the correlation refers only to the latter half of the time series and not throughout the maximum of the CO plume. Because of the time scales used in Fig 13a, the CO and O3 presented do appear to have a phase lag, but this does not hold true when the CO plume is removed and the data are examined over a smaller range of CO mixing ratios. A systematic examination of fire events including sources, and transport paths is warranted but outside of the

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scope of this paper. Both to clarify this discussion and to shorten the publication, we have removed Fig 13a and have included only the latter three examples.

Line 27, page 17640: See the previous comment regarding the negative O3-CO correlation.

Author Response: Figure 12b shows an example from August 9-12, 2005 and the CO and O3 anti-correlation is more clearly illustrated.

Figures: Figure 7: Labels for the color bars are too small, or of too coarse resolution to be readable in my printout. Response: The figure has now been changed to black and white with labeled contours.

Figure 8 caption: Shouldn't "Fig. 12" be "Fig. 6"? Response: Yes, this has been corrected.

Figure 10 caption: Did the authors mean to say "minus" instead of "less" in (a)? In (b) and (c), I suspect "Fig. 11a" should be "Fig. 10a", and in (d) "11c" should be "10c". Response: Corrections made

Figure 13: What are the color schemes for the maps? They are so small that I don't know what I should look for in them. Response: The quality of this figure has been improved, now including the 750 hPa back trajectory superimposed on the analyzed smoke field. This has been added to the caption and the text.

Reviewer 2 comments 1) The authors mention the Mt Bachelor site in central Oregon. However, they do not compare and contrast their measurements with any from that site. Isn't this possible to do? It would be of interest to compare at least the average O3 and CO seasonal cycles.

Author response: For this data period, there are two years of overlap between the Whistler and the MBO data. We have added some discussion about the comparison of seasonally-averaged O3 data from Ambrose et al. (2011), and also CO mixing ratios from Reidmiller et al., (2008).

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2) Exactly how the data are handled is not clear. The authors report standard deviations of the data as a measure of the ambient variability (e.g. Fig. 4), but it is not clear if these refer to standard deviations of 1-minute averages, 1-hour averages, or even daily averages. The averaging period makes a substantial difference in the resulting standard deviations. A clearer explanation of the data treatment is required.

Author response: The reported standard deviations are calculated from the hourly averages. i.e. the mean is calculated from all of the hourly data for a given month for all hours between 2000 and 0800 PST. The standard deviation is calculated from the same hourly averages. This is clarified in the text.

3) A clearer explanation of the uncertainty of the CO measurement is required. Presently (pg. 17630) the information is only: "The detection level was about 19 ppbv and the uncertainty of reported CO concentrations was within _5 ppbv, taken as one standard deviation of the instrument zero." More details of how these numbers were determined are required. Later (pg. 17630) with regard to the average diurnal cycle of CO, the authors state "This change, however, is close to the sensitivity of the instrument and overall, a diurnal variation is not significant on a monthly average." This statement is not clear to me. If individual hourly averages are uncertain to _5 ppbv, and measurements are uncorrelated on a one-day or longer time scale, then averaging over many days should reduce the uncertainty of the average. For example, the seasonal average of 5 years of data for one hour in a diurnal cycle should have an uncertainty of only about _5/(90*5)1=2 or 0.24 ppbv. Hence the diurnal variations in Fig. 3 for CO should be highly significant. These issues require full discussion.

Author response: We have revisited the detection level and the uncertainty and have clarified this discussion in the text. The CO detection level is taken as three times the standard deviation of an instrument zero. The accuracy of the calibration point, taken as three standard deviations of the 100 ppbv point was within 10 ppbv. The larger uncertainty in the CO measurements resulted from the sensitivity of the instrument to changes in operating temperatures. Instrument zeros were done every two hours for

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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 $\pm$ 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. The reviewer's comment on the significance of the diurnal signal is taken and even with the added uncertainty of temperature fluctuations, the uncertainty of the CO diurnal patterns will still be 1 ppbv. The reference to uncertainty of the diurnal cycles is removed from page 17630 and the discussion of the CO patterns has been expanded.

4) The details of the CO hourly averages in Fig. 3 are intriguing, and suggest that there may be a small problem in the data reduction. It appears that there is a strong tendency for the even hour data to be significantly higher than the odd hour data. Is this possibly a result of the zeroing process that took place every two hours through much of the measurement period? There are also only 23 hourly data in the diurnal cycle. What happened to the 24th hour? I suggest that the authors carefully review their data reduction process to see if an error has led to odd-even hour differences, and to the data scatter larger than the 0.24 ppbv precision (see preceding point) expected for a 5 year seasonal average of the diurnal cycle.

Author response: We have checked the data reduction in response to the reviewer's comments. We have looked at the potential effect of averages calculated over the hours with and without the instrument zero and this averaging does not explain the apparent oscillation. We have also checked the effects of temperature oscillations on resulting CO mixing ratios and although this is not a consistent effect throughout the data set, the cycling of the room cooling fan did introduce a regular periodicity in CO

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during multi-week periods in 2005 and 2006. The period of the temperature cycle (<0.5 C) was approximately one hour leading to the cycling observed in Fig 3. Although the noise during these weeks was ± 10 ppbv, on an hourly average, the amplitude is quite constant and the CO mixing ratios are very stable over a 2-3 hour average. For the diurnal patterns, we have modified Figure 3 (now called Fig 2) to separate the diurnal patterns by season and showing O3, CO, and water vapour on each panel. In this figure, the CO data are averages calculated from a data set smoothed with a three-hour running average.

5) The paper is quite long - 43 pages including 13 figures, most with multiple panels. Every opportunity should be taken to make it more concise. In this regard, I do not see that Fig. 1 is required.

Author response: Fig 1 has been removed

6) On page 17629 the authors state "Very little valley influence is expected in winter." A short explanation/justification for this statement should be provided.

Author response: This sentence has been changed to “Very little valley influence is expected in winter as the snow covered surface suppresses convective lifting of the boundary layer to the Peak level.”

7) On page 17631 the authors note that "The observed ozone cycle at Whistler differs from other high elevation sites on the west coast such as Rocky Mountain and Lassen National Parks (Jaffe and Ray, 2007; Jaffe, 2011). 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...." Of course Rocky Mountain National Park is not on the west coast, but more importantly this interesting finding should be more fully investigated. One interesting question is whether US continental pollution is responsible for the summer peak at the US sites, or if it is a latitudinal difference in the Pacific air transported ashore. This could be investigated from coastal sonde data. Sondes launched from Trinidad Head California

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show a broad summer peak at 2 km altitude but not within the marine boundary layer [Parrish et al., 2010]. The 2-km sonde seasonal cycle (presumably representing inflow from the Pacific) is similar to that observed at Lassen National Park. I understand that Environment Canada launches ozone sondes from Kelowna in southern British Columbia. It would be interesting to compare the O3 seasonal cycle from Whistler with that determined from the Kelowna sonde data at an altitude equivalent to Whistler's elevation.

Author response: The reference to Rocky Mountain National Park now is to the Western US, not the west coast. Ozonesonde data from the Kelowna site are now included in the paper (Fig 4c). The ozonesonde data do show the decrease in ozone from spring to summer even though the summer minima are not as low. The monthly averages for the sondes are generally higher than the Whistler Peak monthly averages. For all data grouped by month, the Kelowna sonde ozone is higher than at Whistler by less than 3 ppbv in winter and by 5-8 ppbv in summer. Although the Kelowna flights were in late afternoon, the diurnal variation in O3 at Whistler was not great enough to explain these differences. We agree that detailed comparisons between Whistler and Kelowna data sets will be valuable but that comparison is outside the scope of this paper.

8) On page 17634 the authors state "In summer, the intensifying Pacific High and weakening Aleutian Low cause a more northwesterly flow over the south coast of British Columbia (Fig. 7b)." I can see no hint of that northwesterly flow in Fig. 7b. This discussion should be clarified.

Author response: These figures are replaced with mean sea level pressure to illustrate the Aleutian low and Pacific High in winter and summer.

9) Line 11, pg. 17636 - Can an explanation be given for the large difference seen in Fig. 10a for 2006 compared to the previous 4 years?

Author response: In May 2006, there were more hours related to t-P transport than to NA influences relative to 2003-2005. The increased number of transport events may

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also translate into more intense events although we have not investigated aspect of the dataset directly.

10) Line 20, pg. 17636 - The authors state "During the summer biomass burning period (as represented by August), the amount of ozone in the t-P boxes relative to background is approximately constant at 3–5 ppbv over all of the years (Fig. 10c)." This appears to be incorrect as the quantity actually appears to scatter from -2 to +3 ppbv in Fig. 10c. Also the description of the NA enhancement in 2005 appears quantitatively incorrect. The authors should carefully review all of this discussion to ensure accuracy.

Author response: This discussion has been reviewed and corrected.

11) Line 5, pg. 17637 - The authors mention fires in Alberta as a regional influence. Were the emissions from these fires actually transported to Whistler despite the average? prevailing winds shown in Fig. 7. This should be discussed.

Author response: Yes, transport from the northeast is uncommon. Increases in CO and O3 during mid-June 2002 were coincident with northeasterly back trajectories during period of extensive forest fires in Alberta. This is clarified in the text.

12) Lines 4-8, pg. 17638 - This discussion is not clear. Why should _O3(NA) for 2004 compared to _O3(NA) for 2002 provide an estimate for _O3 from anthropogenic sources?

Author response: The intention was to use delO3(NA) in 2002 as an estimate of NA anthropogenic source contribution to O3 at Whistler. We agree that the statement is unclear and it has been removed.

13) The discussion of Fig. 13 beginning on pg. 17639 must be carefully reviewed, revised and clarified. For example, the authors discuss a strong negative correlation between CO and O3 (slope=-0.21, R2 =0.85) for the first episode (24 June 2004). However, looking at that day in Fig. 13a, there is no obvious negative correlation, certainly not at the R2 = 0.85 level. A much clearer, objective discussion is required in

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regard to the episodes discussed in this figure.

Author response: We have removed the June 2004 period from Figure 13 (now Figure 12). The correlation and slope previously included are for the period following the largest peak in CO. Over the largest CO peak, the CO and O3 are essentially uncorrelated. The discussion now just looks at three periods from August 2005 and September 2006 to illustrate the differences in CO and O3 relationships in fire-affected air masses. Figure 12a now clearly shows an anticorrelation between CO and O3 with a slope of -0.14 and an R2=0.66 whereas Figures 12b-c show periods when CO and O3 were positively correlated. These cases are given to illustrate the variability in the CO and O3 as a result of regional fires.

14) Lines 5-6, pg. 17641 - The authors state that "Both O3 and CO exhibit a seasonal cycle with a spring maximum and summer minimum similar to other background sites throughout the Northern Hemisphere." I am not convinced this is true outside of the marine boundary layer. Elevated sites in Europe exhibit a spring-summer maximum, but that could conceivably reflect regional pollution. A Japanese site (Mt. Happo [Tanimoto, 2009]) does show a strong spring maximum and a summer minimum, but that reflects the seasonal outflow from the East Asian continent, rather than a hemispheric representative feature. Importantly, as noted above, the sondes launched from Trinidad Head show a broad spring-summer maximum above the marine boundary layer. The authors must strongly support their conclusion for the lower free troposphere if they really wish to include this statement. The Canadian ozone sonde record and the Mt. Bachelor data may be useful in this regard.

Author response: We have modified this statement in our conclusions to discuss CO and O3 separately. The text now says: “CO exhibits a seasonal cycle with a spring maximum and summer minimum similar to other background sites throughout the northern hemisphere. O3 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

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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. O3 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 O3 is in JJA and found to be 3.5 ppbv about a daily mean." Over the past year (2010-2011), we have O3 and CO from two additional sites in western Canada – one in the marine boundary layer in British Columbia and one in the Yukon Territory at 1.2 km-asl. Initial data show the absence of this summer peak not only in the marine boundary layer as expected but also at the Yukon site.

Technical issues: 1) Figure 3 caption has "ration" rather than "ratio". This figure caption has been corrected. 2) In Figs. 8 and 9, it would be useful to annotate the curves and symbols with more descriptive labels (e.g. background Pacific, Asian transport, etc.) than the Box number, which requires the reader to refer back to Fig. 6 for an explanation. The figures have been amended. 3) In Fig. 10, the meaning of the red line should be explained in the caption. Area of what burned and where should be clear. This has been clarified in the caption. 4) Line 20, pg. 17637 - "co varies" should be "co-varies" or "covaries". This has been corrected. 5) Line 8, pg. 17636 - The sentence "In May, there is no significant difference between O3 in t-P or NA air masses in 2002, 2003, 2005 ...." I think should also include 2004, i.e. 2002-2005. This description has been updated.

The following references have been added:

Parrish, D.D., K.C. Aikin, S.J. Oltmans, B.J. Johnson, M. Ives, and C. Sweeny (2010), Impact of transported background ozone inflow on summertime air quality in a Califor-

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nia ozone exceedance area, Atmos. Chem. Phys., 10, 10093–10109, doi:10.5194/acp-10-10093-2010.

Ambrose, J.L., Reidmiller, D.R., and Jaffe, D.A.: Causes of high O3 in the lower free troposphere over the Pacific Northwest as observed at the Mt. Bachelor Observatory, Atmos. Environ., 45, 5302-5315, 2011.

Talbot, R. W., J. E. Dibb, B. L. Lefer, J. D. Bradshaw, S. T. Sandholm, D. R. Blake, N. J. Blake, G. W. Sachse, J. E. Collins, Jr., B. G. Heikes, J. T. Merrill, G. L. Gregory, B. E. Anderson, H. B. Singh, D. C. Thornton, A. R. Bandy, and R. F. Pueschel (1997), Chemical characteristics of continental outflow from Asia to the troposphere over the western Pacific Ocean during February-March 1994: Results from PEM-West B, J. Geophys. Res., 102, 28,255-28,274.

Tarasick, D.W., and R. Slater. 2008. Ozone in the Troposphere: Measurements, Climatology, Budget, and Trends, Atmosphere-Ocean, 46(1), 93-115, doi:10.3137/ao.460105.

Heald, C. L., D. J. Jacob, A. M. Fiore, L. K. Emmons, J. C. Gille, M. N. Deeter, J. Warner, D. P. Edwards, J. H. Crawford, A. J. Hamlin, G. W. Sachse, E. V. Browell, M. A. Avery, S. A. Vay, D. J. Westberg, D. R. Blake, H. B. Singh, S. T. Sandholm, R. W. Talbot, and H. E. Fuelberg (2003), Asian outflow and trans-Pacific transport of carbon monoxide and ozone pollution: An integrated satellite, aircraft, and model perspective, J. Geophys. Res., 108(D24), doi:10.1029/2003JD003507.

Please also note the supplement to this comment:
http://www.atmos-chem-phys-discuss.net/11/C10549/2011/acpd-11-C10549-2011-supplement.pdf

Interactive comment on Atmos. Chem. Phys. Discuss., 11, 17621, 2011.

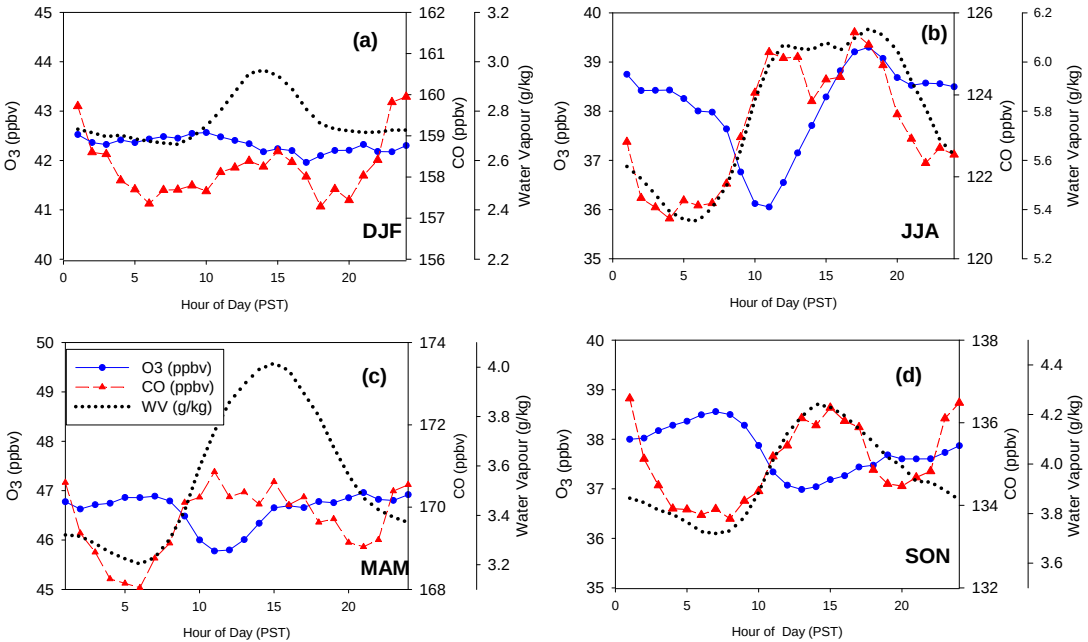

Fig. 1. Diurnal variation in ozone, CO, and water vapour at Whistler Peak 2002-2006 for (a) December-February, (b) June-August, (c) March-May, and (d) September-November.

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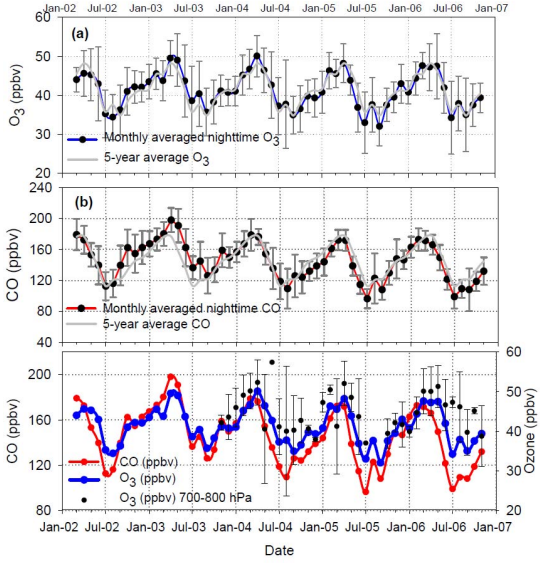

Figure 3: Monthly averages of (a) O_3 and (b) CO nighttime data (1800 – 0800 PST) for Mar 2002 to Dec 2006 at Whistler Peak. Error bars are one standard deviation about the mean of all hourly data. The gray lines show the 5-year averages. (c) Monthly averages of both O_3 and CO from Whistler peak and O_3 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.

Fig. 2.

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