

Interactive comment on “Free tropospheric peroxyacetyl nitrate (PAN) and ozone at Mount Bachelor: causes of variability and timescale for trend detection” by E. V. Fischer et al.

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Response to Reviewer 1 Document Title: Free tropospheric peroxyacetyl nitrate (PAN) and ozone at Mount Bachelor: causes of variability and timescale for trend detection Date: May 9, 2011 We thank all four anonymous reviewers for their thorough evaluation and constructive recommendations for improving this manuscript. Their comments and our responses are listed below. All authors listed on the manuscript concur with submission of the manuscript in its revised form. We have attached a copy of these comments with our responses in italics as a pdf supplement document.

Anonymous Referee #1 General Comments This paper describes multi-year measure-
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ments of PAN at Mount Bachelor Observatory a high altitude site in the NW U.S. These data are of interest and form a potentially useful addition to the literature. The paper has numerous problems, which are serious enough that it is not publishable without significant modifications. The authors seem to REALLY want to be the first to detect an increasing trend in PAN, and they have decided it will be 4%.

This comment suggests that the reviewer does not understand a main thrust of this paper. We do not claim to detect a trend in either O₃ or PAN. Our analysis is different from and complementary to the other recent papers on O₃ trends over the NE Pacific (e.g. Cooper et al., [2010] and Parrish et al., [2009]). The paper adds to an ongoing discussion of how future observations should be deployed so that they could be used detect changes in the composition of air arriving at the North American west coast. Our intent is to lay out the minimum monitoring requirements needed to understand possible trends in O₃ and PAN over North America that could be driven by rising Asian precursor emissions.

So narrow is their focus that they leave out another data set from MBO taken in 2006 [Wolfe et al., 2007] (curiously since the senior author is a co-author on that paper), and do not mention the work of Parrish et al., [2004] who discuss a trend in Eastern Pacific PAN measurements (again curious since the senior author is a co-author on that work as well). Paradoxically, they include a mention of the results of Murphy et al., from the foothills of the Sierra Nevada, which incorporated influences from California urban areas, and in any case, will have different transport patterns than MBO.

We provide readers with a list of the primary references for recent PAN data collected in the Eastern Pacific region, and that list does include Wolfe et al., [2007]. Since confidence in the relative variability between samples is very important for our analysis, we have chosen not to include the Wolfe et al., [2007] observations in the calculation presented in Section 5. We discuss this below in response to the specific comments.

We do agree that the Parrish et al., [2004] paper is worth mentioning. Parrish et al.,

present a reasonable first attempt at revealing changes to the photochemical environment over the NE Pacific. However, our goals are different than the Parrish et al., and we consider the PAN trend analysis presented in Parrish et al. [2004] to have some shortcomings. This is discussed below.

The connection between PAN, and O₃ formation is emphasized several places and the possible Asian influence on both was discussed. Why not include O₃ in this analysis?

O₃ data is included in the analysis (Figure 5 and Table 1).

The relationship between PAN and O₃ is quite complex and may have several features that could result in something other than the simple expected increases that the authors seem to want to focus on. The authors' note that PAN decomposition to NO₂ and subsequent NO_x-drive chemistry can produce O₃ in transported plumes. So one could imagine a scenario in which higher Asian NO_x sources coupled with a warmer troposphere, or lower altitude transport, over the next decade compared to previous years, could result in a larger positive O₃ trend and a negative PAN trend.

We agree that PAN will likely be a mediator of the response of O₃ to changes in climate. There are many plausible future scenarios. Our calculations were repeated with a variety of possible trends in each species, recognizing that the future is unknown.

As has been noted (and will be repeated below) vertical transport is a particular weak point of global models, and GEOS-CHEM is no exception. I think we should prefer to let the atmosphere show us what it is doing and then hope to see if we can capture that with numerical models. With that said, it is useful to see if a trend has been detected and to assess what kind of time-scale would be needed to observe a given trend. I would like to see the paper recast to reflect that the measurements come first, and modeled results should be treated with some skepticism for the afore-mentioned reasons.

We agree. Our focus is to present the measurements and what they tell us about the

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requirements to identify future trends. Uncertainty in the model results were specifically highlighted in the original version of this manuscript. We do not present any new GEOS-Chem results here. Rather we extend our analysis from results that were previously published in ACP.

In response to this comment, we have made edits throughout the text to make it clear that the GEOS-Chem results played a limited role in our analysis. The model was used only as a general guide for past trends, and it is not predictor for future trends (that's why we need to measure PAN). Many factors will influence PAN and O₃ trends including emissions, climate, stratosphere-troposphere exchange, vegetative emissions, etc.

Specific Comments The abstract is too long and contains too much detail.

We have significantly shortened the abstract by removing the discussion of fires and meteorological differences between years.

Pg 4108, line 23, PAN is formed from many VOC precursors, not just acetaldehyde +OH. Indeed, the isoprene => PAN mechanism goes through intermediates such as methylglyoxal.

We have added several additional sentences on the formation of PAN. "The formation of PANs involves several stages of the oxidation of non-methane volatile organic compounds (NMVOCs). Most NMVOCs can serve as PAN precursors though the yield varies (Roberts, 2007). The immediate precursors are the oxidation intermediates acetaldehyde (CH₃CHO), acetone (CH₃C(O)CH₃), and methylglyoxal (CH₃COCHO). Methylglyoxal is an oxidation product of isoprene (Paulot et al., 2009), a very reactive biogenic VOC with a temperature and sunlight dependent emission rate (Guenther et al., 2006). The most abundant Peroxycarboxylic nitric anhydride is commonly called peroxyacetyl nitrate (PAN, chemical formula: CH₃C(O)OONO₂)."

Pg 4109 line 18 The authors are saying increases in PAN and O₃ with are expected because of increasing Asian NO_x. Elsewhere they say that PAN decomposition produces

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O3. Aren't these statements contradictory? See above general point.

No these statements are not necessarily contradictory. The reviewer is confusing long-term versus short term relationships. We have tried to reword the text to make these relationships clear. Briefly, formation of PAN provides a thermally unstable reservoir for NO_x radicals, enabling long-range transport at cold temperatures and eventual release of NO_x in the remote troposphere where these radicals are most efficient at producing O₃.

The authors did not mention the work of Parrish et al., 2004, which is puzzling since the senior author on this paper is also on that paper.

We agree that the Parrish paper is an important work that needs mentioning. However it is also important to recognize the very different goals of our work. The Parrish paper specifically examined PAN trends using an array of data from different locations. Our analysis is focused on documenting and understanding variability at one location. While we do not directly derive PAN trends, our work should be of great interest to researchers interested in understanding these trends.

For those unfamiliar with the Parrish et al. 2004 paper, here are a few important points. The reviewer is referring to Figure 10 in Parrish et al., 2004, which is a plot of previously observed (1985 – 2002) PAN mixing ratios in the eastern North Pacific marine boundary layer. The plot also presents a time series of East Asian NO_x emissions estimated by Streets et al. [2001 and 2003]. This analysis does not end the debate on whether there has been a recent increase in PAN over the eastern Pacific for several reasons. 1) The measurements presented in Figure 10 span a large latitudinal range, with the earliest measurements from the southernmost location. The lifetime of PAN is highly temperature dependent, which provides an alternative explanation for the relationship between PAN and time. The trend line in this figure was drawn using essentially 3 data points. 2) Parrish et al. also point out that the Pt. Arena data was from only 10 days in 1985. Pt. Arena is a surface site. 3) Plumes were intentionally followed in the ITCT

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2K2 campaign, while forecasting support was not available in PHOBEA. The various sampling strategies could also explain the pattern in observed PAN mixing ratios.

We have added a reference to Parrish et al. [2004] to the third paragraph of the introduction where we discuss recent work on O₃ trends over the eastern North Pacific. The PAN data used in Parrish et al., is described in more detail in Roberts et al., (2004), which was already cited in this manuscript. We have also added a reference to Parrish et al. [2004] at the end of Section 5:

“Several previous analyses of O₃ and PAN trends have used data from multiple sites with complex data segregation schemes. This was done due to the fact that no single site existed in this region with long term data (Parrish et al., 2009; Cooper et al., 2010; Parrish et al., 2004). Our analysis suggests that if the true O₃ trend over western North America due to rising Asian precursor emissions is on the order of 1 % per year, it could be corroborated at a site like MBO in a relatively short timeframe with a direct analysis of mean O₃ concentrations. Further information on attribution can be obtained with data segregation techniques and chemical modeling studies.”

The first consistent multi-year measurements – why did Wolfe et al., measurements from MBO during 2006 get left out of this? They included the same time period.

The mean PAN mixing ratio presented by Wolfe et al., was 340 ppbv. We have added a note to Figure 2.

The following sentences are relevant to the calculations presented in Figure 5. The NO mixing ratio in the standard cylinders used to calibrate the 2008 – 2010 PAN measurements was verified through an intercomparison with other cylinders containing a range of NO mixing ratios. This was done for each springtime campaign.

After the Wolfe et al., 2007 paper was published, the NO mixing ratio in the calibration cylinder used in 2006 was found to have drifted to a value less than expected (Glenn Wolfe personal communication). It is impossible to know when the calibration cylinder

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drifted, but there certainly could be a higher uncertainty for these observations than previously thought. Thus we do not want to emphasize this previously collected dataset in this manuscript.

Regardless, one of the motivations for the analysis presented here, is to determine whether a trend in PAN due to rising Asian NO_x emissions would be detected sooner than a trend in O₃. We use observations of both species to show that PAN is more variable than O₃, so a trend in PAN will be more challenging to detect. Adding the Wolfe et al. data to the analysis presented in Section 5 would only increase the variability in PAN, so it would not change the conclusions of this analysis.

4110 – Lines 3-4, these statements are either not true, or are at best misleading.

To avoid confusion, we have removed this sentence from the introduction. However, the statement is explained clearly in Section 3.2 in the following sentences:

“Though aircraft observations have large advantages in understanding the dynamics of individual plumes, which are often intentionally followed, they do not constitute random atmospheric samples. The observations shown in Figure 2 cover a long time span, but the large latitudinal and vertical gradients in PAN mixing ratios make previous data sets insufficient to determine the interannual variability in PAN. Direct comparison is also difficult because time lags between campaigns straddle the springtime maximum in this species (Penkett and Brice, 1986). Spring is a transitional time for PAN. . .”

4111 – Uncertainties seem low. The overall uncertainty should be reported differently. Clearly the overall uncertainty in a measurement that is close to detection limit is larger than 8.2%.

The details of the uncertainty calculation are presented in detail in Fischer et al. (2010), which is why they were not included in the original submission. We have added further details to elucidate exactly what is accounted for in the uncertainty calculations, which we believe to be standard. In response to this comment and the following comment we

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have updated our uncertainty calculation and changed how it is reported. Previously reported uncertainties for PAN-GC systems onboard aircraft are on the order of 15%. In the laboratory setting, which is similar to the constant-altitude and temperature setting of the room that housed the GC at MBO, reported instrument uncertainties are typically better than 10% (Flocke et al., 2005).

Flocke, F., Weinheimer, A. J., Swanson, A. L., Roberts, J. M., Schmitt, R., and Shertz, S.: On the measurement of PANs by gas chromatography and electron capture detection, *J. Atmos. Chem.*, 52, 19-43, 2005.

Additional / Edited text: “We estimate the accuracy of the PAN mixing ratio produced by the calibrator to be 9%. This was calculated as the root sum of the squares of the error in all the calibration components, which includes the reported uncertainty in the mixing ratios of the calibration gases (5.0%), the uncertainty of the flow controllers used to deliver the calibration gases to the calibrator (1.7%, 0.89%, 0.29% for the three flow controllers) and the uncertainty associated with the calibrator efficiency (7.0%). The estimated precision of the system is 3.0%. This is based on repeated sampling from the calibrator at a PAN mixing ratio of 470 pptv. At this mixing ratio, which corresponds to an average peak area of 36 units, the standard deviation of the peak area was 1.1 area units, or 3% of the average area of the repeated samples. We calculated uncertainty as the root sum of the squares of the precision (3%) and the accuracy (9%). We estimate an on-site detection limit of ~15 pptv, and this corresponds to a peak height-to-baseline noise ratio of 3. The uncertainty at levels well above the detection limit is 10%. Since the detection limit is 15 pptv and the median mixing ratio for each campaign was >100 pptv, most observations were well above the detection limit. The average sensitivity throughout the 2008, 2009, and 2010 campaigns was 13.9 + 0.7, 14.1 + 1.3, and 12.1+ 0.9 (mean + 1 standard deviation) pptv per area unit. ”

The authors did not measure the PAN efficiency of their photo-source, but instead use a literature value, what is the uncertainty in that? How would one even put a number on that?

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There are several points to note here: The uncertainty in the efficiency of the calibrator was included in our uncertainty analysis (3% is the reported value for this type of calibrator).

In response to this comment, we reviewed tests performed with the calibrator. 1) In February 2008 we sampled the calibrator outflow using a two-channel chemiluminescence NO_x instrument (see Reidmiller et al., ACP 2009 for a description of the NO_x instrument.) This instrument has 5-minute NO and NO₂ detection limits of 4 and 10 pptv respectively. There was no detectable NO_x in the calibrator outflow. This suggests that the uncertainty should be higher than the 3% reported in the literature. We have repeated our uncertainty analysis using 7% as the uncertainty in the calibrator efficiency and changed the text accordingly.

2) A new Jelight Hg Pen-lamp (285 nm) was purchased and installed in the calibrator prior to spring 2010. Keeping all other settings identical, the PAN produced using the two lamps was injected into the GC. There was no significant change in the size of the PAN peak. This indicates that there was not likely to have been a change in the efficiency of the photo-source over time. Thus we have confidence in the relative differences in PAN from sample-to-sample.

4113 – Line 10 Is this 3-4 days periodicity apparent in the autocorrelation spectrum?

We completed a spectral analysis of the hourly PAN data for each season. There were peaks in the frequency of interest (2-4 days), but these were not significant at the 99% confidence level. Given the relatively short campaigns, this type of analysis is difficult for wave cycles of ~4 days. We added a reference to Fischer et al., (2010b) here to point readers to an analysis of the role of synoptic scale processes in controlling PAN observed at MBO.

Line 16 What is an “event-like” structure? Line 20 You don’t mention what the 1-20 May 2008 average was. Line 23 06:00pm should be 6:00pm

C3038

We have changed the wording here to clarify, and have made suggested changes. This now reads:

“The PAN time series for April 2009 and April 2010 both had more structure than April 2008. The autocorrelation at 1 hour was 0.53 for April 2008, 0.93 for April 2009, and 0.95 for April 2010. PAN mixing ratios below 75 pptv were also much more frequent during April 2008 than in the following years. Consequently the monthly mean for April 2008 was shifted down to 108 pptv as compared to 174 and 150 pptv, for April 2009 and April 2010 respectively. The mean PAN mixing ratio for May 1- 20 2008 (91 pptv) was also lower than 2009 (117 pptv) and 2010 (144 pptv). “

4114 – Wolfe et al. measurements were AT MBO, and spanned the time of year being analyzed in this paper, why is that data not included in this analysis?

See above.

4116 – Line 24 I don’t understand what this sentence means. Do you mean that both 2008 and 2009 had weaker transpacific transport than all the years shown in Fig. 2, except for 2002? The sentence is ambiguous as written.

Yes, this is exactly what was meant. We have re-written these sentences substantially and added specific LRT3 values in response to comments from another reviewer.

4117 – Lines 8-10 This is really unclear, when the author say “the number of hourly trajectory points within a given radius of the latitude and longitude points.” What lat and long points are they referring to? The MBO coordinates? Or have they summed all the trajectory points within a given radius of each lat and long in the hemisphere? (which seems more likely) Line 11-14 I see the difference in Northerly origin, I don’t see the SW aspect. Looking at the color scale, which is in thousands of hours, I realize, I don’t have any idea what Figure 4 is showing, how did the authors get a number in hours?

Is that hours in back-trajectory time, or number of hours out of all the trajectory times? In which case what are the total number of hours?

C3039

Yes, this is exactly what this means. These are trajectory density plots. We have summed the trajectory points within a 200 km radius of each lat and long point in the hemisphere. (As part of our analysis, this type of plot was made with many different radii (100 km, 200 km. . .), which is why "given" was originally used here.) We agree that these sentences could be clearer, and they now read:

"Figure 3 presents a summary of the hourly endpoints from 10-day backward HYSPLIT trajectories. A trajectory was initialized from the summit of MBO each hour for the 50-day period of 1 April to 20 May, thus each plot represents 1200 individual trajectory calculations. These trajectory density plots were created by counting the number of hourly trajectory points within 200 km of each latitude and longitude point. With the goal of highlighting the largest differences in horizontal transport between the spring seasons, the counts were mapped using a log scale. All trajectories were run for the same amount of time, so trajectories crossing longer distances represent faster moving air masses. Figure 3 shows that the relatively high speed transport from the north, that was common in spring 2008 and 2009, was reduced in spring 2010."

The hourly trajectory hourly endpoints were counted, so we have also changed the legend to make this is clear.

Lines 15- 21 How can a paper published in 1996 confirm differences in years 2008-2010? If the author mean that the re-analysis method described in the 1996 publication was used, then say that, and describe where the data came from.

Yes, Kalnay (1996) is the reference for the reanalysis fields. We have clarified these lines:

"The broad features illustrated by the trajectory analysis in Figure 3 are corroborated by NCEP / NCAR reanalysis fields (not shown). We examined composites of the following fields at 700 hPa: geopotential height, temperature, vector winds, and vertical velocity. These fields are produced using meteorological observations from surface sites, ships, rawinsondes, aircraft, and satellites. The data assim-

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ilation system is described by Kalnay (1996), and the data can be accessed at <http://www.esrl.noaa.gov/psd/data/composites/day/>. The 700 hPa geopotential heights confirm more southwesterly geostrophic flow during spring 2010 due to a persistent trough located off the coast. The trough extended from the northern tip of Vancouver Island to central California, and was strongest in early April 2010. It is the most notable feature in the 700 hPa height field distinguishing spring 2010 from spring 2008 and 2009."

4118- Lines 5- 9 I give up. I have no idea what the authors are talking about. What do 22 spatial degrees of freedom mean and how can that be used to derive the confidence limits? Please show your work.

We have added several sentences to clarify how we calculated the confidence intervals and why we believe the confidence intervals are conservative. This paragraph now reads:

'In Figure 4, we have plotted the corresponding vertical distribution of air mass transport to MBO during the three spring seasons. This series of plots was created by averaging the HYSPLIT output for each hour back from MBO. Conservative estimates of the 95% confidence intervals for the means are also shaded. These intervals were calculated taking into account the autocorrelation of the trajectories by using the autocorrelation as observed at the arrival location (MBO). For example, the solid red line in the top plot in Figure 4 is the mean temperature for 720 trajectories initialized in April 2008 (30 days * 24 hours/day). The 720 points at hour 0 are not all independent samples because there is a high degree of autocorrelation from hour to hour, so we cannot use $N = 720$ to calculate a 95% confidence interval around the mean temperature. The trajectory temperature is most correlated at MBO (hour 0) so we used the autocorrelation here to estimate a lower limit to the degrees of freedom. We used Bretherton et al., (1999) to determine the degrees of freedom which was typically 22 for each month containing 720 trajectories initialized from MBO. Thus the confidence intervals surrounding the mean along-trajectory temperature were all calculated using 22 degrees of freedom,

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not 720. For example, middle plot in Figure 4 shows that the average altitude of air mass transport, as calculated by the HYSPLIT trajectories, was higher in 2009 than 2008 and 2010. In contrast, the confidence intervals show that there is no significant difference in transport altitude between April 2008 and April 2010.”

4120 – Lines 1-9 This argument is just plain wrong. The variability in the amount of vertical transport out of East Asia has a huge effect on the amount of PAN that can reach the Eastern Pacific and therefore MBO. This has been shown by previous aircraft studies both in the Eastern Pacific (Nowak et al., 2004, Roberts et al., 2004) and along the continental margin of East Asia (Russo, et al., 2003). It should also be noted that it is precisely this stochastic vertical transport that models, and GEOS-CHEM is no exception, have the hardest time simulating. Assuming that transport is constant is precisely that kind of bias that leads one to believe a modeled result rather to look objectively at the ambient data to see what it actually is.

We agree with the reviewer that the final statement in this paragraph was too strong. We have kept the original references, and have added the suggested references to show that there is not consensus on this point. It should be noted that none of the suggested references, two of which are already cited in this paper, address interannual variability in vertical transport. These lines now read:

“Another factor determining the re-distribution of NO_y is the vertical transport out of the East Asian and European planetary boundary layers. Aircraft campaigns have shown that variability in the amount of vertical transport out of East Asia impacts the amount of PAN that moves downwind (Roberts et al., 2004; Nowak et al., 2004; Russo et al., 2003). However Liang et al., (2005) suggest that transpacific transport is mainly dependent on the meteorology in the eastern half of the Pacific. The passage of mid-latitude cyclones, which are thought to provide the dominant pathways for pollutant export from Asia (Bey et al., 2001), constantly replenish the “pool of Asian pollution in the western Pacific” (Liang et al., 2005). It should be noted that certain scales of vertical transport are difficult to simulate in global chemical transport models.”

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4121 - Line 6 Do the authors have any evidence to back up the statement ‘The Streets et al. (2003) emissions inventory for 2000 underestimated NO_x emissions’?

Zhang et al., (2008) presents a very detailed discussion of the constraints on both the 2000 and 2006 Streets inventories. We have changed this sentence to point readers to the discussion in Zhang et al. The emissions used in global chemical transport models are highly uncertain. Our goal here is to highlight the uncertainties.

Lines 20-21 The auto-correlation numbers presented here mean nothing to me, what would be considered significant? Lines 24-29 There is something wrong here, how does randomly sampling points from the 3 years give a trend with time. It looks like the authors have skipped a step in their explanation, wherein they describe that they mixed in a 4%/year increasing trend. How was this done?

In the top panel of Figure 5 we have randomly sampled the observed 4-day average PAN mixing ratios from Mount Bachelor and added them to a hypothetical +4% per year trend. None of the other 3 reviewers were confused by this section, but we have edited the wording here to make this section as explicit as possible to readers from a variety of backgrounds.

Figure 5 is shown as an example, not as a conclusion. It is possible that the reviewer is confused because he/she missed Table 1. Table 1 presents the results for a range of possible trends, highlighting the uncertainty in model-derived trends. The goal here is not to show that there is a trend in either O₃ or PAN. The goal is to predict how long consistent measurements of PAN or O₃ would need to be done in order to detect a range of plausible trends.

4123- Lines 22-24 The statement ‘There are even fewer observations of PAN, though a trend in this species is expected to be larger and would be significantly easier to attribute.’ seems counter to the conclusion given just above that both O₃ and PAN trends would require about the same time to detect, because PAN is more variable than O₃.

C3043

We agree that the wording here could be improved, but this is not counter to the conclusion above. Based on our current understanding, the trend in PAN is expected to be larger than that of O3. Despite a larger trend in PAN, it may take longer to detect because PAN is more variable. However, if a trend in PAN was detected alongside a trend in O3, this would provide additional evidence that both species were responding to changes in precursor emissions rather than changes in stratosphere-troposphere exchange for example.

Figure 4. It is completely unclear how this figure was generated, and what the unit 'hours' refers to.

We agree that this figure could be better explained. This was addressed above. More details have been added to the text, and the legend has been updated.

Figure 5. The labels are different between the middle and bottom panels, but caption says they are the same. One is 'amgl' the other says 'amsl'. What do those mean?

Thanks for noting a typo in the legend of the bottom plot. The bottom plot should also be 'amgl'. This is "above model ground level". The figure has been fixed, and this has been added to the caption. This term is used in Section 2.2, where the trajectories are described. We have also noted the abbreviation here.

References; Parrish, D.D., et al., Changes in the photochemical environment of the temperate North Pacific troposphere in response to increasing Asian emissions, *J. Geophys. Res.*, 109, 10.1029/2003JD004978, 2004. Russo, et al., Chemical composition of Asian continental outflow over the western Pacific: Results from Transport and Chemical Evolution of the Pacific (TRACE-P), *J. Geophys. Res.*, 108, 8804, doi:10.1029/2002JD003184., 2003. Wolfe, et al., Influence of trans-Pacific pollution transport on acyl peroxy nitrate abundances and speciation at Mount Bachelor Observatory during INTEX-B, *Atmos. Chem. Phys.*, 7, 5309-5325, 2007

Please also note the supplement to this comment:

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<http://www.atmos-chem-phys-discuss.net/11/C3030/2011/acpd-11-C3030-2011-supplement.pdf>

Interactive comment on *Atmos. Chem. Phys. Discuss.*, 11, 4105, 2011.