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Atmospheric Chemistry and Physics
Discussions

Interactive comment on "Analysis of elevated spring-time levels of Peroxy Acetyl Nitrate (PAN) at the High Alpine research sites Jungfraujoch and Zugspitze" *by* S. Pandey Deolal et al.

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We thank reviewer #2 for his/her very competent and extensive review and the valuable comments and suggestions following our replies. (In the supplementary pdf file the comments of the reviewer are written in bold Italics).

Reviewer's comment: This paper reports on a Flexpart cluster analyses applied to two sets of PAN, and associated species measurements at European mountain sites, Jungfraujoch and Zugspitze. While there are multiple years of data for both sites, some after 2008, the period of analysis is limited to May 2008. It is difficult to see how

this paper really advances our knowledge relative to the previous paper by this group, Pandey Deolal et al. [2013], that interpreted data from Jungfraujoch. The case for the value of this paper needs to be made before it is acceptable for publication.

Reply: We agree that the justification of the paper particularly in relation to Pandey Deolal (2013) needs clarification. In the introduction of the revised manuscript we will refer to the recent study of Fischer et al (2014) which compares best available climatology of PAN data (mainly from aircraft measurements) with extensive numerical simulation, being the most comprehensive present PAN study. Fig S2 (Supplementary material) of Fischer et al. (2014) illustrates one of the scientific questions of our study: the sophisticated numerical model which describes aircraft measurements quite well underestimates the PAN spring maxima observed at Jungfraujoch as well as at Zugspitze by more than a factor 2. The large deviation between the GEOS-Chem model simulation (based on a grid resolution of 2° x 2.5o) and measurements might be caused by the not appropriate description of the effect of European emissions for PAN concentration at Jungfraujoch. The study of Pandey Deloal et al. (2013), in which long-range backward trajectory analysis (performed by LAGRANTO using ERA interim wind fields) together with chemical filters was applied covering the years 1997, 1998, 2008, 2009 and 2010 points into the direction that the largest spring-time PAN concentrations observed at Jungfraujoch might originate from European emission of PAN precursors. However, the study of Pandey Deolal (2013) was based on LAGRANTO backward trajectory analysis which utilized coarse meteorological input data and did not describe turbulent and convective vertical transport. Therefore, the study could only provide qualitative and suggestive information regarding the mechanisms responsible for high spring-time PAN concentration at Jungfraujoch. The aim of the present study is to use more adequate transport simulations (FLEXPART with finer resolution input and treatment of turbulent and convective vertical transport) combined with a state-of-the art clustering analysis to verify the tentative interpretation of Pandey Deolal et al. (2013) allowing for a more precise and more detailed description of the involved atmospheric physical processes and their relations. In addition, we extend the analysis by incorporating results from another European high altitude site (Zugspitze) which showed a similar annual PAN cycle as Jungfraujoch. Here we can show that the PAN formation mechanisms are similar for both sites, allowing for a more generalized conclusion than previously for Jungfraujoch only. The representativeness of the results ("case study") of the described mechanism for other years is indeed an important question. In order to further explore the representativeness of the weather conditions encountered in 2008 we compared the transport clusters obtained in our study with a long term weather type classification (also see reply to reviewer 1). The Alpine Weather Statistic (AWS) is a weather classification that was developed to characterise the weather situation at a given time over the Swiss domain (MeteoSwiss 1985: Wanner et al. 1998). The AWS was previously used to analyse PBL transport to JFJ (Henne et al. 2005). The AWS types "convective-indifferent" and "convective-anticyclonic" were identified as weather types for which PBL transport to JFJ was likely during the spring and summer months. Our JFJ cluster 3 largely corresponds with the AWS weather sub-types "convective-anticyclonic flat pressure" and "convective-indifferent easterly advection". The frequency of these two weather types for the years 2001 to 2010 and the months April and May was relatively large in 2008 (>15 days) but comparable to other years (2001, 2004, 2005; > 15 days). When looking at the frequency of all "convective-anticylonic" and "convective-indifferent" weather types, which are likely to allow PBL transport to JFJ, the frequency in 2008 (30 days) was only slightly larger than the average frequency for all years (27 days). Hence, our conclusion on the representativeness of our 2008 case study is twofold. On the one hand, the occurrence of strong PBL influence during easterly flow in May 2008 was exceptional in its persistence and continuation for about 10 days. On the other hand, the frequency of weather types with likely PBL transport towards JFJ was not larger in 2008 than in other years. Therefore, we are convinced that our findings concerning the origin of the pronounced spring time PAN maximum at JFJ are not restricted to the analysed year but can be interpreted in a more general way. We will add this discussion in the revised manuscript. For further discussion why the analysis was restricted to May 2008 see reply to specific comment

below.

Reviewer's comment: In addition, there are a number of general and specific comments that need to be dealt with. General Comments: Contrary to what is stated in the introduction there is a significant PAN background in the northern hemisphere, see for example Roberts [1990] for older data and Fischer et al., [2014] for recent data.

Reply: We agree that the wording of the first sentence about PAN concentrations being close to negligible is wrong (or at least misleading as the sentence was meant to compare ozone and PAN as indicators for photochemical processing and the term "background" itself would need clarification). This first sentence will disappear in a resubmitted manuscript.

Reviewer's comment: The results of the flexpart model need to be assessed in relation to that background.

Reply: We intend to use Figure S2 from Fischer et al (2014) to clarify the scientific question of the study (see above): in this figure "free tropospheric PAN" from a state-of-the art numerical simulation (describing "European free tropospheric air") is compared with measurements at Jungfraujoch and Zugspitze (and we will avoid the term "background" in this context).

Reviewer's comment: Why is only May 2008 being analyzed? There are several other months in that year, and apparently data from 2009 and 2010. Why aren't those time periods being analyzed?

Reply: It is true, that other months of measurements of PAN are available. The selection of May 2008 is justified by the following arguments: During May 2008 JFJ experienced some of the largest hourly PAN mixing ratios ever recorded at JFJ (Pandey Deolal et al., 2013) and also the monthly mean PAN was among the largest on record (see Fig. 2 – this is even more evident in Fig. 2 of the revised manuscript in which PAN data of JFJ of the years 2009 and 2010 are included). PAN at ZSF was comparable to other years. Hence, May 2008 was selected for a more detailed analysis as the variability at the sites can help identifying the potential origin of air masses and meteorological processes involved. FLEXPART simulations for other months are available, but the extended data analysis including footprint clustering is not only time consuming but would also introduce additional, seasonally varying influence factors besides transport when running for an entire year. For example, due to warmer temperatures in summer we may expect a different pattern of PAN advection to Jungfraujoch as during spring. Since largest concentrations and differences to model simulations were observed in spring we wanted to focus on these. In addition, we look at the processes specific for spring condition because these were in the focus of a number of recent publications since many years (see above). For discussion of representativeness of May 2008 see above. Unfortunately, the analysis for May cannot be easily compared with FLEXPART results of other years because the extension not only requires the calculation of the FLEXPART model (such data for other years would be available) but also requires the many other steps of the data analysis which is not a simple task and therefore out of the scope of the paper.

Reviewer's comment: Aren't there a lot of other marker species measured at these sites? Why not use some of those other measurements to track some of the airmass origins?

Reply: It is true that many more trace gas species are measured at Jungfraujoch, however, we thought that the use of the tracers used in this study is sufficient. Balazani Lööv et al. (2008) used the information of more compounds mainly for comparison of trace gas composition at Jungfraujoch with intercontinental transport patterns which is not the aim of the present study as the focus of the present study lies on European scale. Pandey Deolal et al. (2013) compared benzene to ethane ratios with NOy to CO ratios arriving at the conclusion that NOy to CO provides equivalent results to benzene to ethane mixing ratios (particularly when the focus is (only) spring).

Reviewer's comment: There are several PAN data sets from Mountain side/top sites

that show a common meteorological phenomenon, daytime warming of the ground causes upslope flow and nighttime cooling of the ground causes subsidence, pulling air from aloft down to the site. If the PBL height is above the altitude of the site, this usually results in higher PAN at night. Examples of this effect can be found in Roberts et al.,[1995].

Reply: Roberts et al paper (1995) is a valuable reference to discuss the general question of PAN at mountain sites. However, there are also remarkable difference between Whitetop mountain, Virginia, 1680 m above sea level (masl.) in summer and PAN in spring at Jungfraujoch (3680 masl). Even on typical fair-weather days Jungfraujoch is usually not within the PBL, but it is rather only influenced by intermittent injections of PBL air into a secondary Alpine boundary layer (see Henne et al. 2004). This process can usually be seen by elevated late afternoon concentrations of typical primary PBL tracers like CO. Due to the relatively narrow horizontal extent of this injection layer Jungfraujoch comes back under free tropospheric influence during the night again. A strong subsidence during night-time, bringing ozone rich air to the site is usually not observed. Similar arguments can also be given for Zugspitze with the limitation that the Zugspitze observatory is situated approximately 1000 m below Jungfraujoch and, hence, may well be situated within the day-time PBL and night-time residual layer as we explained in more detail for our transport cluster 3. This tendency is also confirmed by the analysis of diurnal variation of ozone at Zugspitze for the month of May for the years 2002 to 2012. In more than 40% of all cases a daily minimum of ozone was observed between noon and the early afternoon, which can be explained with the day-time up-flow of air masses with lower ozone concentrations from the PBL. Nevertheless, in contrast to Whitetop mountain, we don't expect large effects of dry deposition during night-time condition at Jungfraujoch and Zugspitze, since these are rather isolated peaks surrounded by bare rock or ice.

Reviewer's comment: Specific Comments Pg. 12730, Lines 2-3: The statement is made that background concentrations of PAN are "close to negligible" This is simply not true. Depending on latitude, altitude and season, background concentrations of PAN can be several hundred pptv, not negligible relative to the values reported here.

Reply: We agree, that the sentence dealing with "background PAN" is wrong, see above.

Reviewer's comment: Pg. 12730, Lines 10-11: Strange that the authors chose to use a relatively crude model study to make the point about PAN distributions when there are so many actual measurements that can be referenced. The authors could start with the references in Fischer et al., 2014, and if they really want to be thorough there are several review articles and book chapters that could be consulted.

Reply: We will follow the suggestion of the reviewer, i.e. by replacing Moxim et al. (1996) with Fischer et al (2014) in the revised manuscript.

Reviewer's comment: Pg. 12730, Lines 20-23: There are several more key studies of Springtime continental/hemisphere scale transport that describe specific conditions under which PAN and NOy get transported over long distances. These instances involve warm conveyer belt transport associated with frontal passage. See for example Cooper et al., [2001; 2004], and Nowak et al., [2004].

Reply: We will cite these interesting papers (particularly interesting is the study of Cooper et al, 2001 regarding the intercontinental flow for PAN at Jungfraujoch (the NARE 97 study), in which, however, PAN was not included) but note that the scales are different than in the focus of our study (European scale). Conveyor belt transport is indeed very important but not exactly the same process being in the focus of our study.

Reviewer's comment: Pg. 12739 line 15: There is no solid black line in the left panel of Figure 2.

Reply: Thanks for the comment: there really is a mistake in the text. It should read black dashed and red dashed line. It refers to the 1997/1998 data.

Reviewer's comment: Pg. 12741 discussion of thermal decomposition: The net rate

of thermal decomposition depends not just on temperature, but also on NO and NO2. The PA radical will reform PAN through reaction with NO2 unless removed by reaction with NO (or another radical if NO concentrations are low). This can be a substantial correction to the simple thermal decomposition rate.

Reply: We agree that the use of local temperature only allows for a crude estimation of thermal deposition rates, and chemical processes should be mentioned as one potential reason why the correlation is poor – we think that it is outside the scope of the paper to apply e.g. box model simulation (as used e.g. in Henne et al. (2005)) to study this problem in more detail, also because we don't have proper information to explore the chemical process and to verify such a model during transport towards the sites. However, we will add the concerns of the reviewer as a note of caution in the revised manuscript.

Reviewer's comment: Pg. 12742 lines 15-18. There are a lot of examples of PAN-O3 correlations in a whole range on environments, but perhaps most importantly at mountain top sites as noted above.

Reply: We would like to thank the reviewer for this comment. In the meantime, we evaluated the PAN-O3 correlations in more detail and for the individual transport clusters. As a main result we obtained especially large PAN-O3 slopes for the high PAN cluster 3, supporting our hypothesis that these are relatively polluted air masses with considerable NOx available for PAN formation. The obtained slopes are in the same order than those observed in previous studies at the high altitude site Niwot Ridge, CO (Ridley et al., 1990). We will include the PAN-O3 relationship in a revised Figure 8 and include a discussion of the observed slopes and previous findings in the revised manuscript. The more general remark on the overall correlation on p 12742 will be removed.

Reviewer's comment: Pg. 12745 line 12. This statement is wrong, there is an obvious noon maximum in PAN for Cluster 1. It is obvious in the mean but the extent of it is obscured because the standard deviation bars overlap. Ground sites that are in urban areas or otherwise influenced by local emissions have a noontime maximum in PAN.

Reply: It is true, that PAN at Jungfraujoch of Cluster 1 shows a tendency for a systematic diurnal variation (peaking at 12.00, see Fig. 6) but it is not in sync with our strongest PBL tracer: CO. We don't object, that PAN at urban sites often shows peaking values at noon. However, PBL influence (from the Swiss plateau) reaches Jungfraujoch only in the (late) afternoon and emissions in the local surroundings are very small.

Reviewer's comment: Pg. 12746 lines 20-21: The period of high O3 and low water vapor is an obvious stratospheric intrusion, why doesn't the cluster model pick that out? Shouldn't it be left out of the remaining analysis?

Reply: This short event of stratospheric influence was not picked up by the cluster analysis because the latter focused on geographical distribution of surface sensitivities. The stratospheric influence was simulated correctly by the transport model (see Figure S3) but the surface sensitivity map (S3, top-right) showed a rather indifferent distribution. Another reason, why the event was not placed in a separate category by the clustering was our aim to limit the number of transport clusters for a straightforward interpretation. With an increasing number of categories, eventually the event would have been placed into its own category. Due to the shortness of the event we did not think it necessary to manually exclude it from the analysis.

Reviewer's comment: Pg 12747. Line 22. This statement is wrong. The Cluster 3 diurnal profile at JFJ does not show simple daytime injection of PAN into the PBL, rather it shows the classic mountain-top nighttime maxima due to subsidence of PAN-rich PBL air due to nighttime cooling of the surface, hence higher PAN at night.

Reply: We are confused: Do you mean daytime injection of PAN from the boundary layer? It is true that PAN concentration at Jungfraujoch shows an increase until 18.00 which we attributed to transport from the polluted PBL. However, we don't believe, that Jungfraujoch shows "classic mountain-top nighttime maxima due to subsidence of

PAN-rich PBL air due to nighttime cooling of the surface" as PBL does not reach the Jungfraujoch altitude in spring (?). See also the discussion of the high Alpine injection layer above.

Reviewer's comment: Pg. 12748, Lines 8-9. I assume the authors are referring to the washout of the soluble NOy species HNO3 and particle nitrate?

Reply: Yes, this is true. We will clarify this point in a resubmitted version of the manuscript

Reviewer's comment: Pg. 12750, Line 2: The PAN/CO for Cluster 4 was not the highest, Cluster 3 was higher.

Reply: This is actually a mistake in the current manuscript. We will correct this statement in the revised version. It does not change the general interpretation of the PAN/CO ratio for cluster 4.

Reviewer's comment: Figure 2. The colored lines are hard to see. The designation of the black triangles doesn't make any sense, aren't those data already shown by the red line and triangles?

Reply: Thanks for these suggestions. We will revise the figure accordingly.

References:

Balzani Lööv, J. M., S. Henne, G. Legreid, J. Staehelin, S. Reimann, A. S. H. Prevot, M. Steinbacher, and M. K. Vollmer, 2008: Estimation of background concentrations of trace gases at the Swiss Alpine site Jungfraujoch (3580 m asl). J. Geophys. Res., 113, D22305, doi: 10.1029/2007JD009751. Cooper, O., et al., A Case Study of Trans-Pacific warm Conveyor belt Transport: The Influence of Merging Airstreams on Trace Gas Import to North America, J. Geophys. Res., 109, 10.1029/2003JD003624, 2004. Cooper, O.R., et al., Trace gas signatures of the airstreams within North Atlantic cyclones: Case studies from the North Atlantic Regional Experiment (NARE '97) aircraft intensive, J. Geophys. Res., 106, 5437-5456, 2001. Fischer, E.V., et al., Atmospheric peroxyacetyl nitrate (PAN): a global budget and source attribution, Atmos. Chem. Phys., 14, 2679-2698, 2014. Henne, S., M. Furger, S. Nyeki, M. Steinbacher, B. Neininger, S. F. J. De Wekker, J. Dommen, N. Spichtinger, A. Stohl, and A. S. H. Prevot, 2004: Quantification of topographic venting of boundary layer air to the free troposphere. Atmos. Chem. Phys., 4, 497-509. Henne, S., J. Dommen, B. Neininger, S. Reimann, J. Staehelin, and A. S. H. Prevot, 2005: Influence of mountain venting in the Alps on the ozone chemistry of the lower free troposphere and the European pollution export. J. Geophys. Res., 110, doi: 10.1029/2005JD005936. Nowak, J.B., et al., Gas-Phase Chemical Characteristics of Asian Emission Plumes Observed During ITCT 2k2 Over the Eastern North Pacific Ocean, J. Geophys. Res. 109, D23S19, 10.1029/2003JD004488, 2004. Pandey Deolal, S., et al., Transport of PAN and NOy from different source regions to the Swiss high alpine site Jungfraujoch, Atmos Environ., 64, 103-115, 2013. Roberts, J.M., The atmospheric chemistry of organic nitrates, Atmos. Environ, 24A, 243-287, 1990. Roberts, J.M. et al., Relationships between PAN and ozone at sites in eastern North America, J. Geophys. Res., 100, 22821-22830, 1995.

Please also note the supplement to this comment:
http://www.atmos-chem-phys-discuss.net/14/C6904/2014/acpd-14-C6904-2014-supplement.pdf

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Interactive comment on Atmos. Chem. Phys. Discuss., 14, 12727, 2014.