

## ***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 #3 for her/his very competent and careful review and the useful comments and suggestions, following our replies (in the supplementary pdf file the comments of the reviewer are written in bold italics).

Reviewer's comment: The manuscript presents a detailed analysis of meteorological conditions associated with PAN concentrations measured at two high Alpine research sites (Jungfraujoch, Switzerland and Zugspitze, Germany) during May of 2008. The FLEXPART Langrangian Particle Dispersion Model is used to identify transport regimes

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and the PAN measurements are interpreted in light of the 4 or 5 dominant air mass transport pathways. The measurements, co-located with other chemical and meteorological data are of high value to the atmospheric chemistry community, though it seems they have already been published,

Reply: We agree, that the used trace gas measurements of the several sites have been published in other studies. However, we argue that we use them in combination with the transport analysis mainly to illustrate the PBL influence in order to refine the picture as obtained by the cluster analysis.

Reviewer's comment ... and the major contribution of this paper is to extend their interpretation to a detailed analysis for one month. My concerns center mainly around the interpretation of the findings, and if these can be addressed, the paper should be suitable for ACP.

Reviewer's comment: General The use of FLEXPART, which considers turbulent and convective processes, is an advance beyond the earlier work published by the authors which relied on back trajectory analysis. The time scale considered (10 days), however, may be far too short to enable tracing emissions that contribute to raising background PAN concentrations since the PAN lifetime can be at least a few times longer. While the authors find compelling evidence for a European boundary layer influence on the highest observed PAN levels at these sites, the caveat noted in the conclusions section, that a “spring-time increase in the hemispheric PAN background cannot be ruled out from the current analysis” is very important. This limitation of the chosen analysis methods should be emphasized earlier in the paper. For example, P12737-12738 states there is no significant intercontinental transport during this period, could be qualified with ‘rapid’ since transport longer than 10 days is neglected.

Reply: While we agree with the reviewer that the analysed transport could be termed ‘rapid’ and that more emphasize can be put on the fact that we cannot rule out increases in the hemispheric PAN background, we don't think that the incorporation of

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longer backward simulations would change the results of our study. From our experience 10 day backward plumes are usually sufficiently dispersed to represent an average over large parts of the atmosphere. The sensitivity towards specific emissions is decreasing steadily in the backward plume and also becomes more uncertain for longer transport times. In this context we do not think that FLEXPART is a suitable tool to detect PAN precursor accumulation in the hemispheric background. Instead a global scale chemistry transport model such as the one applied by Fischer et al. (2014) needs to be used. In the revised manuscript we also intend to include Fischer et al. (2014) in the introduction as Figure S2 in which state of the art global simulation of GEOS-Chem differ by more than a factor of 2 for PAN measurements of May 2008 at Jungfraujoch and Zugspitze. This discrepancy might point to the difficulty of correct description of the effect of European emission on PAN concentration at the two high alpine sites because such simulations were derived with coarse model resolution of  $2^\circ \times 2.4^\circ$  which is too coarse for proper description of PAN at Jungfraujoch and Zugspitze.

Reviewer's comment: Additional discussion should be included regarding the extent to which PAN to CO ratios can be clearly interpreted as described on P12743-44 in terms of giving differences in production chemistry. How valid is the assumption of a constant CO or PAN background?

Reply: Since we are dealing with relatively short time scales (1 month) and with correlations for individual transport regimes we are convinced that the assumption of a more or less constant background for the initial air mass is justified. This is even true if we consider horizontal and vertical variability of the PAN hemispheric background. Since we look at a specific transport regime at a time the initial air mass will represent an average background concentration over larger areas, but this should still be very similar for all times within the same transport cluster because the area of origin should be similar for all cluster members. Obviously, this assumption is not fulfilled completely and together with limitations discussed in the text leads to the imperfect correlations as observed. We will add a statement in the revised manuscript. From Figure 2 of Fis-

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cher et al. 2014, there appears to be spatial and vertical variability in the hemispheric background. See comment above.

Reviewer's comment:(ACP, 2679-2698; the first author here is a co-author yet this paper isn't referenced here:

Reply: We apologize for not having referenced Fischer et al. 2014 – our paper was on hold for a long period leading to a underrepresentation of the most recent literature. We will include this reference in the revised paper.

Reviewer's comment: Is there not a strong signature of transport history as well? For example, the interpretation seems to assume a fixed ratio in the lifetimes for CO and PAN, but are their lifetimes affected similarly in a warm, moist air mass?

Reply: We believe to have found clear evidence for European scale transport in the analysis, but at this scale we don't believe that the changes in lifetime of CO plays a crucial role and we believe, that (on this short scale) the lifetimes are affected rather similarly in moist air masses, whereas indeed temperature can affect the lifetime of PAN.

Reviewer's comment: To my eye, the clusters for Jungfraujoch and Zugspitze could better align in Figures 4 and 5 as: JFJ 1 with ZSF 2; JFJ 2 with ZSF 3; JFJ 3 with ZSF 4 and JFJ 4 with ZSF 5. Perhaps a simple pattern correlation would confirm that the initial aligning of clusters between JFJ and ZSF is actually strongest? Or that the synoptic conditions are consistent with different transport pathways aloft vs. within PBL? There seems to be a lot of overlap with ZSF 1 and 5. Some discussion as to what unique information is retained in each of these clusters(ZSF 1 versus 5), and why the transport patterns on given days seem different at the two sites would help to clarify.

Reply: We are very grateful to the reviewer for this comment. It helped us identify an error that had happened during the final assembly of these figures (also figures 8, S1 and S2). The clusters for ZSF were not plotted in the correct order. The shown

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cluster 2 for ZSF should have been cluster 1, ZSF 3 should have been ZSF 2, ZSF 4 should have been ZSF 3, ZSF 5 was correct and ZSF 1 should have been ZSF 4. We apologise for this mistake and the confusion it caused. We hope the revised figure will convince the reviewer that no additional pattern correlation analysis is required. As already mentioned in the text, the temporal agreement between JFJ and ZSF clusters is larger than 90 %. For the remaining differences we mainly hold responsible the horizontal distance between the sites and the connected difference in the arrival of synoptic scale systems.

Reviewer's comments: Specific P12746 L22 Is this one stratospheric influence event responsible for the correlation, and if so, perhaps best to exclude it?

Reply: We don't believe that the mentioned very short event of stratospheric influence has a substantial effect on the European scale transport nor the used tracer correlations. The slope of the PAN/CO regression as displayed in Figure 8 and for cluster 2 rather results from the elevated values of PAN and CO directly following the episode of elevated PAN (as explained in current manuscript).

Reviewer's comment: Section 4.2.3 articulates a goal of using the footprint cluster analysis to examine contributions from the free troposphere. From Figure 5, it seems that there are strong influences from the middle free-troposphere in addition to the European PBL.

Reply: We agree with the comment that a substantial effect of the influence of free tropospheric air is suggested in Figure 5. However, we think that this picture is counter-balanced by the results of the correlation analyses that indicated that recent emissions (as detected by elevated CO) must have influenced the air masses.

Reviewer's comment: On P12747, the free tropospheric origin is dismissed as not dominating but why couldn't there be mixing between the PBL and free tropospheric air masses, and thus a combination of transported (longer-lived) PAN and freshly formed PAN?

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Reply: We agree that some contribution from the free troposphere cannot be ruled out completely by the transport analysis. However, we argue that trace gas concentration measurements at the high-altitude sites and the corresponding PBL sites suggest a significant PBL contribution.

Reviewer's comment: P12749 In Cluster 5, are there really not NO<sub>x</sub> sources to the South? Couldn't an equally likely interpretation be that temperatures are too warm in these air masses for PAN to be stable?

Reply: The current formulation might be slightly misleading. Of course there are strong NO<sub>x</sub> emissions south of the Alps in the Po valley. However, average surface sensitivities for cluster 5 were largest within the Alpine area and again towards the Italian coast, while they were relatively small in the Po valley itself. In addition, to this lack of strong fresh emissions (as indicated as well by the lowest observed CO concentrations) also the conditions during transport were not favorable for PAN production since it was mostly overcast (see Figure 9, actually ZSF cluster 5 falls into JFJ cluster 4 in this figure). As mentioned temperatures were relatively large at arrival at ZSF, offering an additional possibility for low PAN contributions as suggested by the reviewer. However, we are not able to deduce the individual contributions in the frame of this study. We will extend the current discussion on cluster 5 in the revised manuscript.

Please also note the supplement to this comment:

<http://www.atmos-chem-phys-discuss.net/14/C6915/2014/acpd-14-C6915-2014-supplement.pdf>

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

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