

1 **Analysis of Elevated Spring-time Levels of Peroxy Acetyl**
2 **Nitrate (PAN) at the High Alpine Research Sites Jungfrauoch**
3 **and Zugspitze**

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17

1 **Abstract**

2 Largest atmospheric peroxy acetyl nitrate (PAN) mole fractions at remote surface sites
3 in the northern hemisphere are commonly observed during the months April and May.
4 Different formation mechanisms for this seasonal maximum have previously been
5 suggested: hemispheric-scale production from precursors accumulated during the
6 winter months, increased spring-time transport from up-wind continents, increased
7 regional-scale production in the atmospheric boundary layer from recent emissions. The
8 two high Alpine research sites Jungfrauoch (Switzerland) and Zugspitze (Germany)
9 exhibit a distinct and consistent spring-time PAN maximum, too. Since these sites
10 intermittently sample air masses of free tropospheric and boundary layer origin, they are
11 ideally suited to identify the above mentioned PAN formation processes and attribute
12 local observations to these. Here we present a detailed analysis of PAN observations
13 and meteorological conditions during May 2008 when PAN levels were especially
14 elevated at both sites. Highest PAN concentrations were connected with anti-cyclonic
15 conditions, which persisted in May 2008 for about 10 days with north easterly advection
16 towards the sites. A backward dispersion model analysis showed that elevated PAN
17 concentrations were caused by the combination of favourable photochemical production
18 conditions and large precursor concentrations in the European atmospheric boundary
19 layer. The results suggest that the largest PAN values in spring 2008 at both sites were
20 attributable to regional-scale photochemical production of PAN in the (relatively cold)
21 planetary boundary layer from European precursors whereas the contribution of inter-
22 continental transport or free tropospheric build-up was of smaller importance for these
23 sites.

24 **1. Introduction**

25 Peroxy acetyl nitrate (PAN) is a key compound of reactive nitrogen species (NO_y)
26 formed by photooxidation and has a significant effect on the global distribution of
27 tropospheric ozone (Fischer et al., 2014). PAN plays an important role in the complex
28 radical chemistry of the troposphere because it acts as a relatively long lived reservoir
29 for nitrogen oxides (NO_x) and reactive organic radicals. At cold temperatures PAN can

1 be transported over long distances and, hence, contribute to inter-continental transport
2 of O₃ precursors (Penkett and Brice, 1986;Nielsen et al., 1981;Rappenglück et al.,
3 2010;Schrimpf et al., 1998;Tsalkani et al., 1991). It is well known that PAN exhibits a
4 strong seasonal cycle, peaking in spring in the northern hemispheric remote
5 atmosphere (Moxim et al., 1996). These PAN spring maxima were often explained in
6 the following way: the mixing ratios of long-lived NMVOC (non-methane volatile organic
7 compounds) accumulate in the free troposphere (FT) over the winter season due to less
8 efficient photo-degradation (Penkett et al., 1993); in early spring photochemistry
9 becomes active and the accumulated NMVOC in the northern FT foster the build-up of
10 PAN and O₃ leading to the observed maximum in both species in the background
11 troposphere (Penkett and Brice, 1986;Monks, 2000;Zanis et al., 2007;Fenneteaux et al.,
12 1999;Zanis et al., 2003). The seasonal pattern indicated by these studies leads to the
13 perception that the spring maximum is not directly influenced by recent emissions into
14 the planetary boundary layer (PBL) but is a background air phenomenon. In contrast,
15 there are other studies explaining PAN spring maxima in terms of long range transport
16 or special meteorological situations (Fischer et al., 2010;Ridley et al., 1998) or a
17 combination of both free tropospheric and PBL air masses (Bottenheim et al., 1994).

18 PAN measurements reported during the period 1987-1988 from three Swiss sites
19 (suburban station, Dübendorf, 431 m asl; forest site, Laegeren, 685 m asl; Alpine valley
20 site, Davos, 1630 m asl) showed significant seasonal variation in PAN with elevated
21 monthly mean values in spring for all the stations, suggesting that maximum PAN
22 concentrations were associated with anti-cyclonic weather types and low wind speeds
23 (Wunderli and Gehrig, 1991). Previous PAN observations at the Swiss high Alpine site
24 Jungfrauoch (JFJ) revealed maximum PAN levels > 1 ppb in spring-summer season
25 and attributed the maxima to thermally-induced transport from the PBL (Zellweger et al.,
26 2003).

27 Based on the above discussion there are three hypotheses for the origin of the PAN
28 spring maximum at remote and high altitude sites in Europe:

- 1 (a) increased background concentrations: build-up of precursor during winter in the
2 northern hemisphere, active photochemistry producing high PAN concentrations in
3 spring in the free troposphere;
- 4 (b) boundary layer influence and meteorologically favourable situations: transport from
5 the boundary layer, e.g. by convective transport and/or accumulation in anti-cyclonic
6 air flow;
- 7 (c) inter-continental transport: increased background mixing ratios (for e.g. ozone) from
8 inter-continental transport during spring as shown by recent studies (Cooper et al.,
9 2001;2004;2010;Fiore et al., 2009).

10 Fischer et al. (2014) used sophisticated numerical simulations that described aircraft
11 measurements quite well but underestimated the PAN spring maxima at the Alpine sites
12 Jungfraujoch (Switzerland) and Zugspitze (Germany) by more than a factor 2 (see their
13 Fig S2). The large deviation between these GEOS-Chem simulations (based on a grid
14 resolution of $2^\circ \times 2.5^\circ$) and measurements might be caused by the not appropriate
15 description of the effect of European emissions for PAN concentration at Jungfraujoch.
16 The study of Pandey Deolal et al. (2013), in which long-range backward trajectory
17 analysis (performed by LAGRANTO using ERA interim wind fields) together with
18 chemical filters was applied covering the years 1997, 1998, 2008, 2009 and 2010 points
19 into the direction that the largest spring-time PAN concentrations observed at
20 Jungfraujoch might originate from European emission of PAN precursors. However, the
21 study of Pandey Deolal et al. (2013) was based on LAGRANTO backward trajectory
22 analysis which utilized coarse meteorological input data and did not describe turbulent
23 and convective vertical transport. Therefore, the study could only provide qualitative and
24 suggestive information regarding the mechanisms responsible for high spring-time PAN
25 concentration at Jungfraujoch.

26 The aim of the present study is to use more adequate transport simulations (FLEXPART
27 with finer resolution input and treatment of turbulent and convective vertical transport)
28 combined with a state-of-the art transport categorization to verify the tentative
29 interpretation of Pandey Deolal et al. (2013) allowing for a more precise and more
30 detailed description of the involved atmospheric physical processes and their relations.

1 In addition, we extend the analysis by incorporating observations from another
2 European high altitude site (Zugspitze) which showed a similar annual PAN cycle as
3 Jungfrauoch. Here we can show that the PAN formation mechanisms are similar for
4 both sites, allowing for a more generalized view than previously for Jungfrauoch only.
5 We limit the analysis to the month of May 2008, when particularly large PAN mole
6 fractions were reported at both sites. In addition, observations from nearby elevated
7 rural sites (Rigi and Chaumont (Switzerland) and Hohenpeissenberg (Germany)), which
8 are more representative for the day-time PBL, are used to further interpret the
9 processes responsible for the build-up of large PAN mole fractions.

10 **2. Site characterization and measurements**

11 The main sites used in this study (Jungfrauoch and Zugspitze, but also the PBL site
12 Hohenpeissenberg) are so called “global stations” of the Global Atmosphere Watch
13 (GAW) programme of the World Meteorological Organization (WMO), while the two
14 additional Swiss sites are regional (Rigi) and contributing (Chaumont) stations to GAW.
15 For all sites detailed measurement and site information can be found in the GAW station
16 information system (GAWSIS, <http://gaw.empa.ch/gawsis>). The Swiss sites are also
17 part of the Swiss National Air Pollution Monitoring Network (NABEL), which is operated
18 by the Swiss Federal Laboratories for Materials Science and Technology (Empa) in
19 collaboration with the Swiss Federal Office for Environment (FOEN) (Empa and FOEN,
20 2013). The measurements at Zugspitze are supported by the Federal Environment
21 Agency (UBA) and regular monitoring of meteorological parameters and atmospheric
22 radioactivity is performed by the German Weather Service (DWD). Continuous
23 measurements of relevant gaseous species and aerosols are performed at all sites. An
24 overview of all the sites is provided in Tab.1 and their locations are shown in Fig. 1.

25

1 **2.1 Site characterization**

2 **2.1.1 High Alpine sites - Jungfraujoch (JFJ) and Zugspitze (ZSF)**

3 The observatory at Jungfraujoch (Sphinx observatory, 3580 m asl) is situated between
4 the Mönch and the Jungfrau mountains in the Bernese Alps of Switzerland. The site is
5 intermittently influenced by the lower FT and European PBL air and, therefore, provides
6 the opportunity to characterize air masses with very different origin and air mass history.
7 Air arriving from the north is often influenced by surface contact over the Swiss plateau
8 before reaching JFJ, while air masses arriving from the south are often advected from
9 the Po Valley crossing the inner Alpine region (Parker et al., 2009; Zellweger et al.,
10 2003).

11 The Zugspitze Schneefernerhaus (ZSF, 2670 m asl) observatory is situated in southern
12 Germany at the northern rim of the Alps. Therefore, it is suitable for the detection of air
13 masses advected from the north (Kaiser et al., 2007). The measurement station is
14 situated on the southern slope of Zugspitze between the summit and a skiing area.
15 Normally, Zugspitze receives free tropospheric air but, similar to JFJ, the site is
16 frequently exposed to boundary layer air in summer time due to thermally-induced flow
17 systems (Gantner et al., 2003; Reiter et al., 1987). In comparison to JFJ, a stronger
18 influence of surface emissions on the trace gas observations at ZSF was deduced and
19 the site was placed into a different category ("weakly influenced") as JFJ ("mostly
20 remote") in a study categorising remote air quality sampling sites in Europe (Henne et
21 al., 2010). The altitude difference between the two sites is about ~ 900 m, while the
22 horizontal distance is around ~ 250 km.

23 **2.1.2 PBL sites – Hohenpeissenberg (HPB), Rigi (RIG) and Chaumont (CHA)**

24 The Hohenpeissenberg observatory (HPB) is another GAW site located in Germany,
25 about 40 km north of Zugspitze in a hilly area dominated by agriculture and forests. The
26 site is predominantly situated in the day-time PBL and night-time residual layer as it is
27 located on top of a small mountain (985 m a.s.l.) and about 300 m above the
28 surrounding area.

29 The station Rigi (RIG) (1031 m asl) is situated on the northern slope of the Rigi
30 mountain, in an elevated rural environment 600 m above Lake Lucerne. The site is

1 surrounded by grass-land and forest areas and small cities such as Zug and Lucerne
2 are approximately 12 km away from the site and at considerably lower elevation. Rigi is
3 located about 65 km north-east of JFJ. The Chaumont observatory (CHA) (1136 m asl)
4 is located about 700 m above Lake Neuchatel. The area is dominated by meadows and
5 pastures. The city of Neuchatel is situated about 5 km south of the station, but well
6 below at the lake shore. The station is located about 90 km north-west of JFJ. Both
7 Swiss sites can be expected to be within the day-time PBL during the spring and
8 summer months, while they are more decoupled from lowland influences during night
9 and winter.

10 **2.2 Trace gas measurements**

11 **2.2.1 Jungfrauoch (JFJ)**

12 The air was sampled from the main inlet dedicated for trace gas observations, which
13 has a total length of about 3 m, with 2 m on the roof top and 1 m inside the laboratory.
14 The inlet consists of stainless steel tubing with an inner diameter of 90 mm and is
15 constantly heated to 10 °C. The air flow rate was 50 m³/hour. The PAN instrument was
16 directly connected to the main inlet using PFA tubing. Since PAN measurements are
17 sensitive to temperature, the instrument was placed close to the main inlet avoiding
18 further heating to laboratory temperatures.

19 PAN measurements were performed at JFJ using commercial gas chromatograph (GC)
20 analyzer and a calibration unit provided by Meteorologie Consult GmbH (Metcon). The
21 technique is based on chromatographic separation with subsequent detection and
22 quantification by an electron capture detector (ECD). For more details see Pandey
23 Deolal et al. (2013). Other trace gases such as total reactive nitrogen species (NO_y),
24 nitrogen oxides (NO_x), CO and O₃ are routinely monitored as part of the NABEL
25 monitoring network (Empa and FOEN, 2013). NO_y, NO_x and NO measurements at JFJ
26 were performed using high sensitive analyzers (ECO physics CLD 89p) based on a
27 chemiluminescence technique. More details are presented in Pandey Deolal et al.
28 (2012). CO measurements were performed using a commercially available instrument
29 (APMA-370, Horiba) based on non-dispersive infrared absorption (NDIR). Ozone was
30 measured using a commercially available monitor (Thermo Environmental Instruments,

1 Model 49C, UV absorption). The measurements of CO and O₃ are described in more
2 detail in Zellweger et al. (2003;2009).

3 **2.2.2 Zugspitze (ZSF)**

4 The air was sampled with the UBA steel inlet used for measuring reactive gases. The
5 total length of the inlet is 3.5 m with 2.25 m on the roof top and 1.25 m inside the
6 laboratory. A borosilicate glass tube was placed inside the steel inlet with inner glass
7 diameter of 80 mm. The inlet is constantly heated to + 6°C. The air flow rate was 22.9
8 l/min.

9 PAN measurements at ZSF were performed using the same technique and instrument
10 as described for JFJ measurements. NO_y and NO measurements were performed using
11 CRANOX, ECO physics (2x CLD 770 AL pptv) containing a gold converter and two
12 reaction chambers. The gold converter is heated to 300° C with 2% CO (99.997%, Air
13 Liquide). NO_x was measured as NO after the photolytic conversion by the photolytic
14 converter (PLC 760 MH) instrument. The converter efficiency of the gold converter
15 mainly ranged between 95 - 98% and conversion efficiency of PLC ranged from 61 to
16 82%. The detection limit for NO_y and NO channel was 50 pptv. The time resolution of
17 these measurements was 145 seconds. Calibrations were performed twice a week. The
18 typical drift of the calibration span signal for NO during four days was 1.1-1.4%

19 **2.2.3 Hohenpeissenberg (HPB)**

20 PAN measurements at this site were started in the late 1990's and continued till
21 present, using the same equipment as for JFJ and ZSF. Additionally the PAN
22 measurements at HPB have been quality tested by at a blind inter-comparison
23 experiment at NCAR, Boulder, CO (Tyndall et al., 2005). Long term analysis of CO,
24 nitrogen dioxide (NO₂) and O₃ time series was reported by (Gilge et al., 2010) where
25 these measurements were also compared with other Alpine sites JFJ, ZSF and Hoher
26 Sonnblick.

2.2.4 Rigi (RIG) and Chaumont (CHA)

A variety of trace gases and aerosol parameters (such as NO₂, O₃, particulate matter and volatile organic compounds (VOC)) as well as meteorology are routinely performed at Rigi and Chaumont (Empa and FOEN, 2013).

3. Transport analysis

3.1 Backward dispersion simulations

The Lagrangian Particle Dispersion Model (LPDM) FLEXPART (Version 8.1) (Stohl et al., 2005) was used to calculate source receptor relationships (SRR) for May 2008 measurements for the two high Alpine sites. For each 3-hourly interval 50'000 particles were released at each receptor site (JFJ and ZSF) and traced back in time for 10 days considering the mean flow, turbulent PBL flow and deep convection. The model was driven by European Centre for Medium Range Weather Forecast (ECMWF) operational analyses (00, 06, 12, 18 UTC) and forecasts (03, 09, 15, 21 UTC) with 91 vertical level and a horizontal resolution of 1° by 1° for the global domain and 0.2° by 0.2° for a nested domain covering the Alpine area (4° W - 16° E, 39° - 51° N). Compared to the aforementioned study by Pandey Deolal et al. (2013), which drew its conclusions from single trajectory simulations, the present transport simulations are better suited to quantitatively capture the influence of the European PBL on the observations at the high Alpine sites since FLEXPART explicitly simulates turbulent and convective mixing that cannot be represented in single-trajectory models.

Release heights of 3000 m and 2500 m were chosen for JFJ and ZSF, respectively. This is significantly lower than the true altitudes of the observatories and takes into account the limited horizontal resolution of the model, by which the Alpine topography is not well represented, requiring a release height somewhere between the station's real altitude and the model ground (Brunner et al., 2012; Keller et al., 2012).

The simulated SRRs allow directly linking a mass release at a source grid cell with a mass mixing ratio at the receptor (Seibert and Frank, 2004). SRRs are given in units $\text{s m}^3 \text{ kg}^{-1}$ and are also referred to as footprints and emission sensitivities. SRRs were generated on a regular grid with 0.1° by 0.1° covering Western Europe (Fig. 4) and a

1 secondary grid with 0.5° by 0.5° horizontal resolution covering the larger North Atlantic
2 region (see Fig. S1 in the supplementary material). The vertical resolution of both grids
3 was restricted to 10 levels up to 15 km above model ground, the lowest of these with a
4 100 m thickness above ground.

5 **3.2 Footprint clustering**

6 In order to see the effects of different flow regimes on PAN concentrations, simulated
7 SRRs were classified into different flow regimes applying clustering methods to the
8 transport simulations but not to the observed trace species. A straightforward approach
9 would be to treat the SRR in every cell of the output grid as an individual time series in
10 the cluster analysis. However, in that case the number of variables would become too
11 large to be handled efficiently and arbitrary results might be produced due to the
12 inclusion of grid cells with very small SRRs. Therefore, we reduced the number of grid
13 cells by aggregating cells with small average (May 2008) emission sensitivities to larger
14 grid cells. Starting from grid cells with 0.1° resolution we allowed aggregation to grid
15 cells with up to 3.2° horizontal resolution. Only SRRs in the lowest output level were
16 considered. This grid reduction is similar to the method that was used in regional
17 inversion studies where it is beneficial to reduce the dimension of the inversion problem
18 (Vollmer et al., 2009; Keller et al., 2011). We iteratively varied the SRR threshold for grid
19 aggregation to obtain approximately 100 grid cells (cluster variables) for the calculation
20 of the dissimilarity matrix required by the clustering algorithm. Only the European
21 domain was considered for the clustering, which will focus the separation of flow
22 situations more onto the continental scale transport to the sites and to a lesser degree
23 onto the inter-continental transport. However, as will be discussed in Section 4, the
24 model results for May 2008 did not suggest any significant inter-continental transport
25 from North-America during this period and, hence, the focus on the European domain is
26 justified in this case. Since the time series of aggregated SRRs were not normally or
27 log-normally distributed, we chose an alternative distance measure to obtain the
28 dissimilarity matrix, \mathbf{D} with elements d_{ij} . Instead of the usually applied Euclidean
29 distance we calculated distribution independent absolute distances between the ranks
30 of the SRRs within the time series

$$d_{ij} = \sum_{l:1,N} \left| \text{rank}(SRR_l)_i - \text{rank}(SRR_l)_j \right|, \quad (1)$$

2 where index l runs over all times N and i and j refer to the individual grid cells. Here rank
3 stands for the sample rank of values in a vector. If ties (same values within vector)
4 existed these were given an average rank. Once the dissimilarity matrix is formed, the
5 clustering was done using k-medoids clustering (Kaufman and Rousseeuw, 1990). The
6 number of clusters was obtained using the silhouette technique (Kaufman and
7 Rousseeuw, 1990) by choosing the number of clusters (in the range 2 to 20) for which
8 the average silhouette widths became maximal. The technique described here is similar
9 to the one presented by Hirdman et al. (2010) for Arctic sites and essentially the same
10 as applied by (Sturm et al., 2013) to FLEXPART simulations for JFJ for a period of three
11 years.

12 The clustering was applied to the time series of the aggregated emission sensitivities for
13 both high Alpine sites separately. For JFJ the maximal silhouette width was at 4
14 clusters, while for ZSF the situation was more complicated. Here the overall maximum
15 silhouette width was obtained for 18 clusters, which gave a much too fine separation of
16 the transport situations. Other local maxima were at 3 and 5 clusters. The clustering
17 with 5 clusters was more similar to the one obtained for JFJ. Hence, 5 clusters were
18 retained for ZSF.

19 For each cluster, average surface SRRs were calculated by summation over all cluster
20 members and division by the number of cluster members N_c

$$21 \quad RTC_{i,j,k}^c = \frac{\sum_{l \in C} SRR_{i,j,k,l}}{N_c},$$

22 where i, j, k represent the spatial indices and l the temporal. The index c identifies the
23 cluster number.

4. Results and discussion

4.1 Seasonal cycle of PAN

PAN measurements from different sites are shown in Fig. 2. At JFJ, PAN measurements were performed during campaigns in 2008 for the spring - summer (May and August) and autumn (September and October) months. The monthly mean mixing ratios of PAN for both JFJ and ZSF are presented in Fig. 2, left (left panel). These measurements indicate a strong seasonal cycle in the PAN with peaking mole fractions in late spring (April or May) and minima in the autumn and winter months. Prior to recent measurements, PAN observations at JFJ from April 1997 - May 1998 (black solid line) also revealed a similar annual cycle (Zellweger et al., 2000). PAN measurements at JFJ performed during campaigns between February 2005 and August 2006 (black crosses) by Balzani Lööv et al. (2008) indicated background mole fractions < 0.2 ppb in April and May however, spring mean mole fractions were found significantly lower than all other reported measurements. Campaign measurements during February/March 2003 at JFJ showed mean concentrations of 0.142 ppb (Whalley et al., 2004), which is in agreement with the observations from other years Fig. 2. (right panel) shows the PAN measurements at the PBL sites including HPB and the Swiss sites Dübendorf (suburban), Lageren (rural forest) and Davos (Alpine valley, 1630 m asl) taken from Wunderli and Gehrig (1991). All these measurements in the PBL, also including the Alpine valley site, clearly show the same seasonal behaviour and are in line with previous observations of spring PAN maxima at northern hemispheric mid-latitudes (Penkett and Brice, 1986; Monks, 2000; Zanis et al., 2007; Zanis et al., 2003; Fenneteaux et al., 1999). The only exception showing a summer maximum are the measurements of HPB in 2003 which is most probably caused by the special conditions of the European heat wave in summer 2003 (e.g. Ordonez et al., 2010). The larger interannual PAN variability (even excluding 2003) at the PBL sites as compared to the high altitude sites can be explained by the stronger influence of variable meteorology on observed mole fractions close to the precursor emissions. Also note that the site Davos is a relatively remote site compared to the other PBL sites, explaining part of the suggested large interannual variability.

1 During May 2008 JFJ experienced some of the largest hourly PAN mixing ratios ever
2 recorded at JFJ (Pandey Deolal et al., 2013) and also the monthly mean PAN was
3 among the largest on record (see Fig. 2). PAN at ZSF was comparable to other years.
4 Hence, May 2008 was selected for a more detailed analysis as the variability at the sites
5 can help identifying the potential origin of air masses and meteorological processes
6 involved.

7 Since high Alpine sites intermittently receive FT and PBL air, it should be possible to
8 attribute high PAN observations to either the FT or PBL, if the air mass contributions
9 can be clarified. Even on typical fair-weather days Jungfraujoch is usually not within the
10 PBL, but it is rather only influenced by intermittent injections of PBL air into a secondary
11 Alpine boundary layer (see Henne et al., 2004). This process can usually be seen by
12 elevated late afternoon concentrations of typical primary PBL tracers like CO. Due to
13 the relatively narrow horizontal extent of this injection layer JFJ comes back under free
14 tropospheric influence during the night again. A strong subsidence during night-time,
15 bringing ozone rich air to the site as observed at other, lower elevation mountain sites
16 (Roberts et al., 1995) is usually not observed at JFJ or ZSF, with the limitation that the
17 ZSF observatory is situated 910m m below JFJ.

18 **4.2 Observations in May 2008**

19 **4.2.1 Meteorological conditions**

20 The entire month was characterized by an alternation between rather stagnant high and
21 low pressure systems over Europe. A low pressure system with its centre over the North
22 Sea and the UK prevailed from the beginning of the month until 5 May. From 6th - 11th
23 May, distinct high pressure conditions developed over southern Scandinavia extending
24 south- and eastward towards Central and Eastern Europe. This resulted in high
25 irradiation and cloud free conditions in Central and parts of Eastern Europe and this
26 period was considered as blocking anti-cyclonic conditions (Hamburger et al., 2011).
27 Towards the end of this period pressure gradients weakened and the deep convection
28 potential increased resulting in local thunderstorms over the Alps and Jura mountains
29 on 12th of May. From 13th - 17th May the situation over Central and Western Europe was
30 dominated by a low pressure system moving from the Gulf of Biscay towards northern

1 Germany. The Alpine area was influenced by the frontal systems embedded in this
2 lower pressure system. As a result, irradiation (cloud cover) was reduced (enhanced)
3 south and west of the Alps. A south foehn situation developed on 15th and 16th of May
4 with precipitation on the southern side of the Swiss Alps. From 17th to 31st May, low
5 pressure conditions persisted over Central Europe leading to a succession of frontal
6 passages.

7 **4.2.2 Observations at Jungfraujoch and Zugspitze**

8 The time series of trace gas observations at JFJ and ZSF are shown in Fig. 3 for May
9 2008. The PAN mixing ratios at JFJ were especially high during the period 6 - 15 May
10 reaching a 3-hourly maximum of 1.2 ppb. PAN was elevated during the same period at
11 ZSF as well, but did not exceed 1 ppb.

12 In addition to PAN, other trace species such as NO_y, CO and O₃ showed increased
13 mixing ratios during this period at both sites as well, while NO_x mixing ratios remained
14 comparably low (Fig. 3). After 15 May PAN levels dropped at both sites and remained
15 between 0.1 and 0.5 ppb for the rest of the month.

16 In general PAN levels were lower (factor 0.7) and NO_x and NO_y levels were greater
17 (factor 2.9 and 1.4, respectively) at ZSF as compared to JFJ. The monthly average
18 contribution of PAN to total NO_y was about 59% and 26% for JFJ and ZSF, respectively.
19 Part of this difference may be related to the temperature difference between the sites
20 and the connected difference in thermal decomposition of PAN. The average
21 temperature of +1.5° C and -5.0° C at ZSF and JFJ, respectively, during the high PAN
22 episode can be translated to average PAN lifetimes with respect to thermal
23 decomposition of $\tau = \sim 1$ day and $\tau = \sim 5$ days for ZSF and JFJ, respectively.
24 Temperature differences were reduced between 20th May and 24th May but strongly
25 increased after. However, overall a weak negative correlation (Pearson correlation
26 coefficient: $R = -0.17$) was observed between PAN differences and temperature
27 differences between the sites. This is an indication, that temperature is only one factor
28 influencing the PAN to NO_y ratio which also depends on NO, NO₂ and organic radical
29 availability during air mass aging, but could not be quantified in detail in the scope of
30 this study.

1 O₃ levels were generally greater at JFJ as compared with ZSF and specific humidity
2 was generally smaller, most likely due to the higher altitude of the JFJ observatory. An
3 exception to this observation is the period 3 May to 6 May, when the lowest O₃ mole
4 fractions occurred during May 2008 at JFJ. At the same time CO levels were decreased
5 and humidity increased. Unfortunately, PAN measurements are missing for 4 May to 6
6 May at JFJ and, when looking at the PAN decrease on 3 May, it can only be assumed
7 that PAN levels were low as well (supported by the fact that NO_y mixing ratios remained
8 low, too). Trace gas mole fractions at ZSF did not show any special event during the
9 same period. Furthermore, an episode of high NO_x mole fractions was observed at ZSF
10 on 21 and 22 May, which is also reflected in relatively low O₃ mole fractions at the same
11 time and site.

12 **4.2.3 Footprint cluster analysis**

13 To further analyse the conditions that led to the observed variability in PAN
14 observations and especially the period of elevated PAN the trace gas time series were
15 split into different categories according to the transport clustering described above
16 (footprint clustering). Since the clustering is based on transport history of the observed
17 air masses only, it is thought to shed light on the main question of this article as to
18 which extent the observed spring maximum in PAN can be related to free tropospheric,
19 hemispheric background scale production of PAN from accumulated precursors or
20 regional scale production from recent emissions.

21 As described above, the clustering resulted in 4 and 5 clusters for JFJ and ZSF
22 respectively. The results of the clustering in terms of temporal attribution can be seen in
23 Fig. 3, in which the time series were coloured according to the transport cluster. It can
24 directly be seen that the individual clustering at the sites resulted in relatively similar
25 temporal cluster attributions at both sites. When considering that clusters 4 and 5 at
26 ZSF could actually be joined to be comparable to cluster 4 at JFJ, the detected
27 transport regimes match between the sites in 91 % of all cases. Keeping in mind that
28 the clustering relies on the simulated transport history only and not on the in-situ
29 observations, it is remarkable that the clustering excellently separates the episode of
30 elevated levels from periods with low PAN. This in itself already indicates that large

1 parts of the PAN variability actually depend on the transport history and may be
2 explained by analysing the conditions during the different transport regimes in detail.

3 In the following, the observed time series are further interpreted following the obtained
4 transport clustering. The results of the latter are displayed in Fig. 4 and Fig. 5 as cluster
5 average surface SRRs and cluster average latitude-altitude SRR distributions for the
6 European domain, respectively. Similar Figures for the larger North Atlantic region can
7 be found in the supplementary material (Fig. S1 and S2). In addition to the observed
8 trace gas time series, the observations were split by transport cluster and aggregated to
9 average diurnal cycles (Fig. 6 and Fig. 7). Where available, parameters from the less
10 elevated sites, usually residing in the PBL or night-time residual layer, were treated in
11 the same way, using the clustering as obtained for the nearby high Alpine site. For JFJ
12 the average from the Swiss PBL sites (CHA and RIG) was taken, while for ZSF the
13 observations from HPB were used as PBL reference. Observed PAN – CO, and PAN –
14 O₃ relationships at the high Alpine sites, again disaggregated by transport cluster, are
15 depicted in Fig. 8. Regression slopes were calculated from 3 hourly data using weighted
16 total least square regression (Krystek and Anton, 2007), which takes the measurement
17 uncertainty of both variables into account.

18 In a simplified way correlations between CO and PAN can be understood as follows.
19 Assuming a constant PAN and CO background, emissions will lead to an initial increase
20 in CO and PAN precursors in an air mass. During transport from the source to the
21 receptor PAN may be produced under favourable conditions while CO can be assumed
22 to remain relatively constant. During transport the original pollution “plume” will further
23 mix with background air masses. The interception of different degrees of mixed air
24 masses at the receptor will then result in correlation between CO and PAN spanning the
25 range between the two endpoints of background conditions and pollution plume. The
26 stronger the correlation the closer this simplified view actually matches reality, while
27 weak correlations may indicate both: minor PAN production and/or ill-defined pollution
28 plumes. In this study we analysed correlations for well-defined transport regimes and a
29 relatively short period of time. Hence, the background for each transport regime is
30 thought to be relatively constant and correlations should be robust. The steeper the
31 slope between PAN and CO the more efficient PAN was produced in the original plume.

1 Similarly, PAN – O₃ slopes can be an indicator of how efficient PAN was produced in
2 comparison to O₃ production. It can be expected that PAN production is more efficient in
3 very polluted air masses (or fresh emission plume) and becomes less efficient for less
4 polluted air masses (or older plume) (Roberts et al., 1995).

5 Finally and to foster the interpretation in terms of vertical mixing and local
6 photochemical production, cluster average afternoon (12 and 15 UTC) PBL heights and
7 daytime (06, 09, 12, and 15 UTC) cloud cover maps for Central Europe were derived
8 from ECMWF-IFS operational analysis and forecast data, the same as used for the
9 transport simulations (Fig. 9). PBL heights were derived by applying a critical
10 Richardson number criterion (Vogelezang and Holtslag, 1996).

11 The individual transport clusters can be described as follows:

12 **Cluster 1 (Westerly advection).** The SRRs in this cluster indicate a cyclonic flow from
13 the North Atlantic region passing over the Iberian Peninsula and France before reaching
14 JFJ and ZSF (Fig. 4 and Fig. 5 and supplementary material S1 and S2). Additional
15 influence from the western Mediterranean was identified for ZSF. While in general
16 westerly advection with descending flow dominated this cluster, mainly representing air
17 masses from lower tropospheric levels, sampled air masses had occasional PBL
18 contact over France, Switzerland and, in the case of ZSF, southern Germany (Fig. 4,
19 right panel). The influence of surface emissions was larger for ZSF than JFJ, as
20 indicated by greater SRRs for the first. This category was experienced during an
21 uninterrupted period from the beginning of May to 5 May. PAN concentrations were
22 relatively low, in the range between 0.2 - 0.5 ppb at ZSF but dropped below this range
23 at JFJ from 3 May onwards (Fig. 3). This coincides with a period of decreased CO and
24 O₃ at JFJ (see above). From the presented continental scale SRRs the difference in
25 transport patterns between JFJ and ZSF is not apparent. However, when looking at the
26 SRRs for the larger northern hemisphere (see supplementary material Fig. S1 and S2) it
27 becomes clear that in the case of JFJ parts of the air masses summarized in this
28 transport regime actually originated over the southern North Atlantic, were transported
29 northward over the Atlantic and finally advected towards Europe. This partially tropical
30 origin could explain the relatively low mole fractions of CO and O₃ as observed at JFJ

1 during the second half of this transport regime. Similar transport events towards JFJ
2 were previously reported by (Bond et al., 2011), who documented the influence of
3 advection from low northern latitudes on molecular hydrogen, methane and CO. Primary
4 pollutant concentrations in this cluster were generally low. Occasionally high O₃ mixing
5 ratios may indicate the influence of higher altitude air masses. At both sites, no
6 pronounced diurnal cycle was observed for PAN, NO_y or NO_x, while a weak afternoon
7 increase in CO and specific humidity could be seen for JFJ. NO_x, CO and specific
8 humidity differences between the PBL and the high Alpine sites were larger for JFJ
9 suggesting a larger degree of decoupling of the site from the PBL as in the case of ZSF
10 (Fig. 6 and Fig. 7). According to model derived average afternoon PBL heights both
11 sites were influenced by PBL air in the afternoon (Fig. 9). Cloud cover was rather large
12 in the region that air masses passed prior to arrival at JFJ, indicating moderate
13 photochemical turnover in these air masses. For ZSF air masses had a less direct
14 transport path from the west and showed surface contact also in regions that were more
15 cloud free (south-western Germany, south-western France). These observations also
16 agree with the estimated regression slopes of PAN to CO (Fig. 8) that were steeper for
17 ZSF than JFJ indicating less efficient PAN production in the air mass that reached JFJ.
18 Overall the PAN/CO slope exhibited moderate values in this cluster. In summary, the
19 observed conditions were not favourable of regional scale PAN production from recent
20 emissions for JFJ, but indicated recent production for ZSF due to increased emission
21 contact of the sampled air masses.

22 **Cluster 2 (Recirculating north-easterly/south-westerly advection).** This flow regime
23 comprises air masses that mainly arrived from north-easterly directions with additional
24 surface influence south-west of the sites (Fig. 4 and Fig. 5). This is not the consequence
25 of overlaying two separate transport regimes at different times, but is also characteristic
26 for most of the individual SSRs during this period. The core of the backward plume
27 typically moved slowly south-westward before taking a north-easterly and ascending
28 path. Finally, part of the plume was recirculated westwards at higher altitudes and
29 detrained into the PBL again, causing increased surface emission sensitivities west of
30 the sites. The surface footprint for JFJ in the Fig. 4 indicates relatively large emission
31 sensitivities over the western Alps and France, the easterly component is more

1 pronounced for ZSF with strong sensitivities along the northern flank of the Alps in
2 Austria and Bavaria. The regime occurred on 5 and 6 May and again between 18 and
3 25 May. This cluster showed considerable PBL contact in agreement with high water
4 vapour content as observed at the sites. PAN mole fractions at both sites remained
5 moderate for most of the category (~0.4 and 0.3 ppb for JFJ and ZSF, respectively).
6 However, JFJ experienced a few hours of high PAN on 6 May which fell into this cluster
7 and caused the late afternoon peak in the overall diurnal cycle for this cluster (Fig. 6).
8 Average daytime cloud cover was relatively large in this category (Fig. 9) suggesting
9 weak photochemical activity and, hence, little potential for regional scale photochemical
10 production of PAN from recent emissions. This is also supported by the insignificant
11 correlations between PAN and CO as observed at ZSF and the relatively small PAN/CO
12 slope at JFJ (Fig. 8). Again, the large PAN/CO correlation at JFJ results from the
13 measurements on 6 May that were not typical for this cluster. Furthermore, trace gas
14 observations on 23 May at JFJ suggested a short phase of stratospheric influence (high
15 O₃, low CO and humidity, see Fig. 3), which was not encountered at ZSF. This is
16 supported by the dispersion calculation that indicates air originating from the tropopause
17 region over north-western France (see supplementary material Fig. S3) but the surface
18 sensitivity map (S3, top-right) showed a rather indifferent distribution (S3, top-right).
19 This short event of stratospheric influence was not picked up by the cluster analysis
20 because the latter focuses on the geographical distribution of surface sensitivities.
21 Another reason, why the event was not placed in a separate category by the clustering
22 was our aim to limit the number of transport clusters for a straightforward interpretation.
23 With an increasing number of categories, eventually the event would have been placed
24 into its own category. Due to the shortness of the event we did not manually exclude it
25 from the analysis.

26

27 **Cluster 3 (Easterly advection).** The SRRs in this cluster describe typical anti-cyclonic
28 conditions with easterly to north-easterly advection and descending air masses. In
29 addition, a southerly component close to the sites caused enhanced surface emission
30 sensitivities in northern Italy and Switzerland for JFJ and Austria and to a smaller
31 degree northern Italy for ZSF (Fig. 4). From Fig. 5 it can be seen that during this period

1 free tropospheric air masses descended in the anticyclone. However, air masses had
2 contact with the PBL shortly before reaching the sites, as can be seen by the relatively
3 focused surface SRRs (Fig. 4). By far the highest pollutant concentrations were
4 observed in this cluster including maxima for PAN, NO_y, NO₂, O₃ and CO. The
5 descending air flow in this category may suggest that the observed PAN was mainly of
6 free-tropospheric origin. However, the following considerations against this hypothesis
7 can be made. First, next to PAN also CO was elevated at both sites. While part of this
8 CO may have been produced in the free troposphere from VOC and CH₄ degradation, it
9 seems more likely that it stems from direct surface emissions. Second, the decreased
10 cloud cover over southern Germany and Eastern Europe (Fig. 9) favoured PBL
11 photochemical production of PAN from fresh emissions in the PBL. Third, PAN levels at
12 ZSF were as high as at the nearby PBL site HPB (Fig. 6). No diurnal cycle of PAN was
13 observed at ZSF and the model estimated daytime PBL top was well above the sites
14 altitude (Fig. 9), both suggesting that ZSF was completely within the daytime PBL and
15 remained within a residual layer during the night. This is in contrast to the usually
16 intermittent PBL influence observed at high altitude sites, caused by the injection of PBL
17 air into the FT over Alpine terrain (Henne et al., 2004; De Wekker et al., 2004). If ZSF
18 was completely situated within the PBL or residual layer it is more likely that PAN was
19 recently produced from fresh emission than from increases in hemispheric background
20 levels. Fourth, PAN was larger at JFJ as compared to ZSF and showed a diurnal cycle
21 typical of day-time injections of PBL air (Fig. 6). This is also supported by a similar
22 diurnal cycle in CO and specific humidity. No systematic diurnal cycle was observed for
23 O₃ at JFJ, most probably due to the fact that afternoon O₃ mole fractions were similar in
24 the PBL as indicated by the observations at CHA and RIG (where night-time values
25 were decreased due to surface deposition, see Fig. 6). PAN production in such PBL
26 injections can be very efficient since large amounts of fresh precursors (NO_x and
27 peroxyacyl radicals) are available and the air mass is adiabatically cooled during the
28 injection, moving the NO₂-PAN balance towards PAN (Henne et al., 2005a). The
29 average PAN/CO slope at JFJ was 0.023 as compared with 0.016 at ZSF (see Fig. 8),
30 suggesting that additional, rapid PAN production took place when PBL air. The relatively
31 small correlation coefficient at JFJ (0.56) as compared to ZSF (0.75) may indicate

1 various levels of PAN production efficiencies in different PBL injections. At night-time
2 PAN levels at JFJ were comparable to those at ZSF or even fell under those at ZSF (8
3 and 9 May, see Fig. 3). NO_y levels were comparable for both sites. However, the
4 PAN/ NO_y ratio was larger at JFJ, which again indicates fresh PAN production, since no
5 precipitation occurred in this regime, which could have washed out NO_y (remember that
6 the water soluble HNO_3 is an important species in the class of NO_y). Precursor levels in
7 the PBL adjacent to JFJ were actually larger (NO_x 3-5 ppb) as compared with HPB (<2
8 ppb). For JFJ large emission sensitivities over the western Po Valley were estimated.
9 The western Po Valley including the metropolitan area of Milan comprises large
10 anthropogenic emissions of NO_x and VOCs (e.g. Prevot et al., 1997) and weak
11 ventilation conditions favour the accumulation of pollutants. In addition, large amounts
12 of biogenic VOC emissions occur within the Alpine region and may deliver the amount
13 of peroxyacyl radicals required for strong PAN production.

14 In summary, these observations point towards a regional scale production of PAN in the
15 PBL, which may further be enhanced when PBL air masses are lifted into the lower FT,
16 where they were sampled at JFJ.

17 **Cluster 4 (South-easterly advection).** Fig. 4 shows that air masses combined in this
18 cluster had only weak surface contact, mainly close to the sites within the Alps and over
19 Italy and the adjacent parts of the Mediterranean. The respective air masses remained
20 within the lower FT north of 30° N prior to arrival at the sites (see Fig. S1 and S2 in the
21 supplementary material). This flow pattern occurred during two episodes in May 2008,
22 namely 15 – 18 May and 26 – 31 May. For ZSF two transport clusters were present
23 during these periods, the second one is described below. The current cluster showed
24 low PAN mean concentrations of 0.2 – 0.4 ppb and also experienced rather low other
25 trace gas concentrations (NO_x , NO_y , CO). No diurnal cycle in any of the trace species
26 was observed at either site, compared to close-by PBL sites (Fig. 6). Hence, the
27 influence from recent emissions on these air masses was considered small. Recent
28 photochemical processing in these air masses was probably low due to relatively large
29 cloud cover over the Alps and Northern Italy. The PAN/CO slope at JFJ was almost as
30 large as for cluster 3. However, this was mainly caused by the attribution of high PAN
31 levels on 15 May to this cluster. This day was the last of the high PAN episode and

1 probably better related to cluster 3 than to the current transport cluster. Without the data
2 from 15 May correlation coefficient and slope considerably decreased. Similar
3 arguments can be made for ZSF, where PAN mixing ratios were still large on 15 and 16
4 May, which were assigned to the current cluster, but probably should have been
5 assigned to the high PAN cluster (3).

6 **Cluster 5 (Southerly advection (ZSF only))**. This SRR describes the transport path
7 from the South, with moderate SRRs over the Mediterranean and Italy and additional
8 boundary layer contact in the Alpine region. While there are large NO_x sources
9 especially in the western part of the Po Valley, a close look at the surface sensitivities
10 (Fig. 4i) reveals that these were most likely not intercepted by the air masses in this
11 cluster, which showed larger emission sensitivities only in the Alpine area north of the
12 Po Valley and again south of the Po Valley. In line with the transport simulations, PAN,
13 NO_y, and CO mixing ratios were the lowest in this cluster. Due to the southern, low
14 tropospheric origin of the air masses, these were relatively warm and moist as
15 compared to the other transport clusters. While the correlation between PAN and CO
16 was the strongest of all clusters, the regression slope was the smallest (Fig. 8),
17 indicating inefficient PAN production, most likely due to the lack of available NO₂ and
18 photochemical production (cloudy conditions during transport; see Fig. 9h).

19 **4.2.4 Correlation between PAN and ozone**

20 Fig. 8 (bottom) shows PAN vs. ozone correlations for the individual clusters.
21 Correlations between PAN and O₃ mole fractions contain valuable information of the
22 production of the two photo-oxidants integrated over the time since the release of the
23 primary pollutant. Very large slopes up to 0.1 were reported from the Los Angeles basin
24 for fall 1980 (Grosjean, 1983) representing highly polluted air masses, particularly very
25 high NO_x concentrations. The relation between the slopes of PAN vs. O₃ with air
26 pollution loadings was demonstrated from day-time measurements during summer 1987
27 at the rural site Niwot Ridge, CO, USA (Ridley et al., 1990). The PAN to O₃ slope was
28 0.048 for polluted air (up-slope flow from easterly directions), but was 5 times smaller
29 for westerly advection of less polluted air. Roberts et al (1995) found slopes around
30 0.0242 in campaign measurements from rural sites in eastern US in summer 1988,

1 which also can be compared with the slopes of our study though the physical conditions
2 of our Alpine mountain sites are not directly comparable with those of the summer
3 campaigns in US.

4 In our study the highest slopes were found in cluster 3 (Easterly advection) (see Fig. 8).
5 At JFJ PAN vs O₃ the slope was 0.057 supporting our result that PAN was enhanced
6 because of recent contact with polluted PBL air (Fig. 6). At ZSF the slope in the same
7 cluster was lower (0.038), indicating less favourable PAN production condition than for
8 JFJ. Lowest PAN-O₃ slopes were observed for cluster 1 (Westerly advection) at JFJ
9 (0.017) and cluster 2 (Recirculating north-easterly/south-westerly advection) at ZSF (<
10 0.017). In these air masses contact with recent polluted planetary boundary layer was
11 found to be small, also resulting in low NO_x mole fraction.

12 **4.2.5 Representativeness of spring 2008**

13 In order to further explore the representativeness of the weather conditions encountered
14 in spring 2008, we compared the transport clusters obtained in our study with a long
15 term weather type classification. The Alpine Weather Statistic (AWS) is a weather
16 classification that was developed to characterise the weather situation at a given time
17 over the Swiss domain (MeteoSwiss, 1985;Wanner et al., 1998). The AWS was
18 previously used to analyse PBL transport to JFJ (Henne et al., 2005b). The AWS types
19 “convective-indifferent” and “convective-anticyclonic” were identified as weather types
20 for which PBL transport to JFJ was likely during the afternoon of spring and summer
21 months. Our JFJ cluster 3 largely corresponds with the AWS weather sub-types
22 “convective-anticyclonic flat pressure” and “convective-indifferent easterly advection”.
23 The frequency of these two weather types for the years 2001 to 2010 and the months
24 April and May was relatively large in 2008 (>13 days) but comparable to other years
25 (2007: 15 days; Fig. S4a). When looking at the frequency of all “convective-anticyclonic”
26 and “convective-indifferent” weather types, which are likely to allow PBL transport to
27 JFJ, the frequency in 2008 (30 days) was only slightly larger than the average
28 frequency for all years (27 days; Fig. S4b). Hence, our conclusion on the
29 representativeness of our 2008 case study is twofold. On the one hand, the occurrence
30 of strong PBL influence during easterly flow in May 2008 was exceptional in its

1 persistence and continuation for about 10 days. On the other hand, the frequency of
2 weather types with likely PBL transport towards JFJ was not larger in spring 2008 than
3 in other years. Therefore, we are convinced that our findings concerning the origin of
4 the pronounced spring time PAN maximum at high Alpine sites are not restricted to the
5 analysed year but can be interpreted in a more general way.

6

7 **5 Conclusions**

8 In agreement with previous studies PAN measurements from ZSF and JFJ showed a
9 pronounced seasonal cycle with maximum mole fractions in late spring. This indicates
10 that the spring maximum of PAN in background air masses as observed at other
11 northern hemispheric sites is also a typical phenomenon at high Alpine sites. The origin
12 of the spring-time maximum at the two Alpine sites was evaluated in more detail for May
13 2008 when PAN levels at JF were especially large. Different transport regimes towards
14 the sites were distinguished using a clustering method on backward dispersion
15 simulations. These show that air masses in May 2008 had recent PBL contact in
16 different parts of Europe before reaching the measurement stations at JFJ and ZSF. At
17 both sites, the highest PAN concentrations of May 2008 were connected with
18 descending air masses in anti-cyclonic flow (cluster 3). However, these air masses
19 experienced pronounced contact with the PBL under photo-chemically favourable (cloud
20 free) conditions, prior to the arrival at the sites. Comparison with nearby PBL sites
21 reveal that the ZSF observatory was situated within the day-time PBL, while JFJ was
22 influenced by PBL injections during this period. PAN levels were considerably lower
23 during all other flow regimes also for those less influenced by recent PBL contact.
24 Therefore, we conclude from our study that under the conditions as sampled at two high
25 Alpine European sites, PAN spring maxima is mainly caused by the following factors:
26 (1) high pressure conditions lead to an accumulation of trace gases in the PBL and
27 vertical transport from the PBL becomes important for transporting the pollutants to the
28 sites (2) solar irradiance is already large in May which enhances the photochemistry
29 during cloud free conditions as encountered during the anti-cyclonic transport regime (3)

1 temperatures are still relatively low in the lower free troposphere preventing thermal
2 decomposition of PAN which becomes more important in summer.

3 The analysis of the high spring PAN mixing ratios at these Alpine sites clearly suggests
4 that the spring maximum is primarily caused by PAN production in and export from the
5 regional PBL. Highest PAN observations during May 2008 were not connected with free
6 tropospheric conditions, but with PBL air masses. These results agree well with those of
7 Pandey Deolal et al. (2013) that, based on hemispheric scale backward trajectories,
8 indicate that those air masses which had surface contact in the European boundary
9 layer were associated with largest PAN and NO_y mixing ratios in spring and are
10 attributable to European boundary layer sources and not inter-continental transport or
11 free tropospheric production. However free tropospheric background and
12 intercontinental transport also make a significant contribution as PAN mole fraction in
13 such air masses without recent contact with European PBL were found to be around
14 0.20 to 0.25 ppb (see Pandey Deolal et al., 2013) which is in rather good agreement
15 with an estimate from the present analysis as averaged PAN concentration from
16 Cluster 1 (most typical for long-range transport) was 0.278 whereas PAN concentrations
17 of cluster 3 most relevant for European PBL advection were around 0.8 ppb. The
18 presented analysis is restricted to one single month, however, analysis of respective
19 synoptic condition according to alpine weather statistics show that this and similar
20 weather condition are common for European spring condition, and therefore we may
21 conclude that the appointed mechanism for the PAN spring maxima is typical also for
22 other years.

23 **Acknowledgment**

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27 and Gornergrat (HFSJG) for providing access to Jungfrauoch facilities and respective
28 custodians for their support. We are thankful to NABEL for their data, which is operated

1 by Empa in collaboration with the Swiss Federal Office for the Environment. We also
2 thank MeteoSwiss for provision of meteorological data from Jungfrauoch.

3

1 **Table**

2

3 Table 1. Characteristics of measurement sites: high Alpine sites (Jungfrauoch, JFJ and
 4 Zugspitze Schneefernerhaus, ZSF), which are intermittently within the free troposphere
 5 (FT) and influenced by boundary layer injections, and elevated rural sites
 6 (Hohenpeissenberg, HPB; Rigi, RIG; Chaumont, CHA), which are usually situated within
 7 the day-time planetary boundary layer but well above the night-time inversion layer. The
 8 given temperature and ambient pressure levels give the range of the observations in
 9 May 2008.

10

Parameter	Jungfrauoch (JFJ)	Zugspitze/ Schneefernerhaus (ZSF)	Hohenpeissenberg (HPB)	Rigi (RIG)	Chaumont (CHA)
Country	Switzerland	Germany	Germany	Switzerland	Switzerland
Geographical coordinates	46.33° N 7.59° E	47.42° N 10.98° E	47.80° N 11.02° E	46.07° N 8.45° E	47.02° N 6.58° E
Altitude (m asl)	3580	2670	985	1031	1137
Temperature (K)	260 - 274	266 – 285	277 – 300	276 – 297	274 – 295
Pressure (hPa)	647 – 662	727 – 742	895 – 912	890 - 907	879 – 895
Category	High Alpine (FT/PBL)	High Alpine (FT/PBL)	Elevated rural (PBL)	Elevated rural (PBL)	Elevated rural (PBL)
Measurement operation (trace gases)	Empa	UBA	DWD	Empa	Empa

11

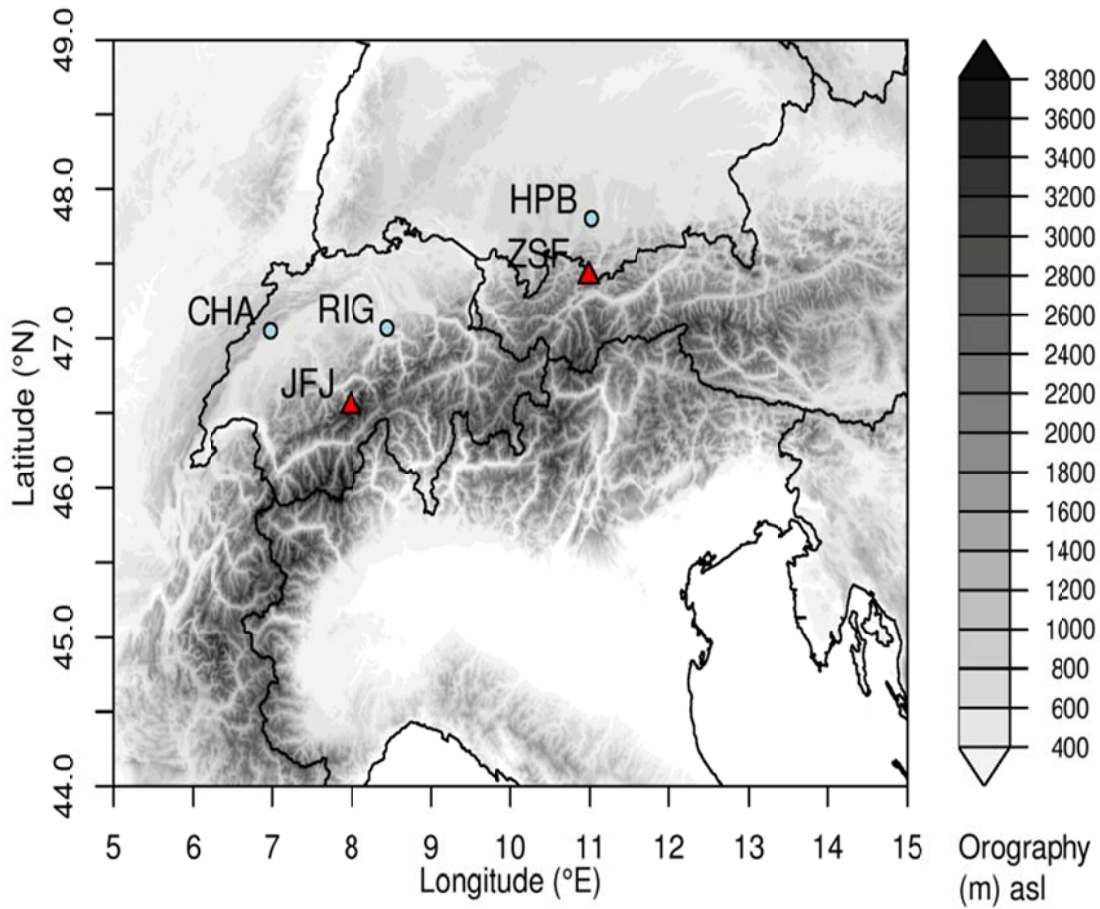
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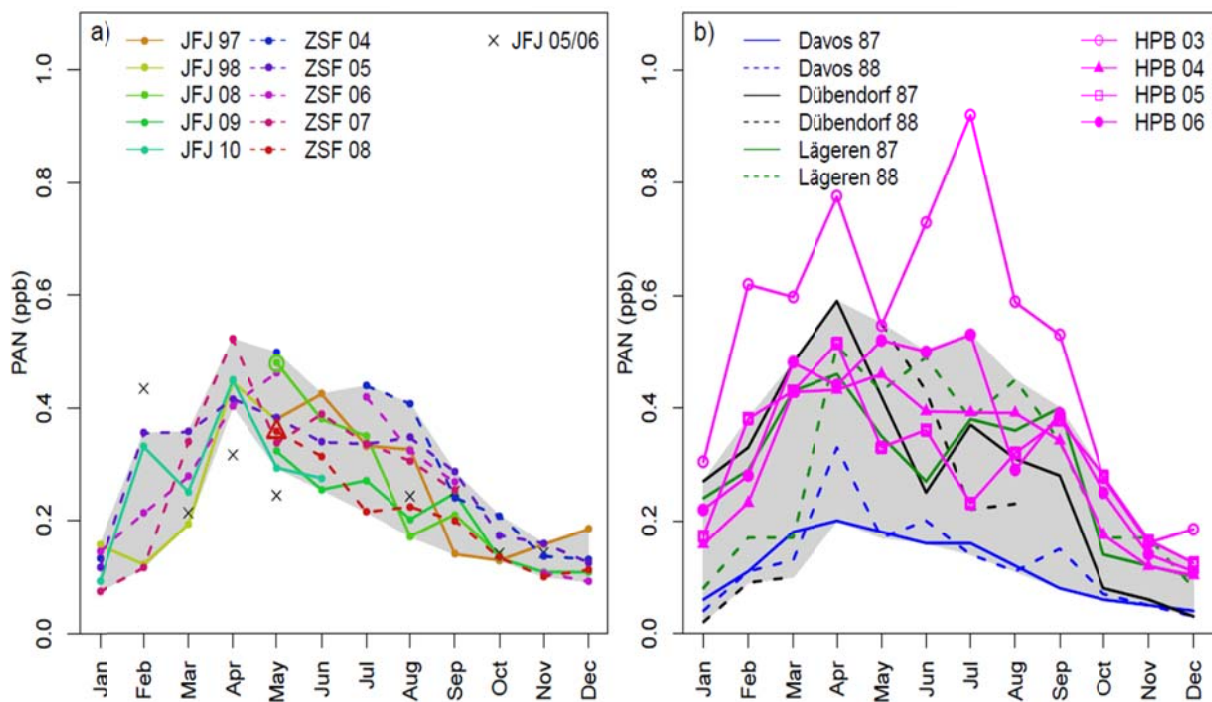
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1 **Figures**



2

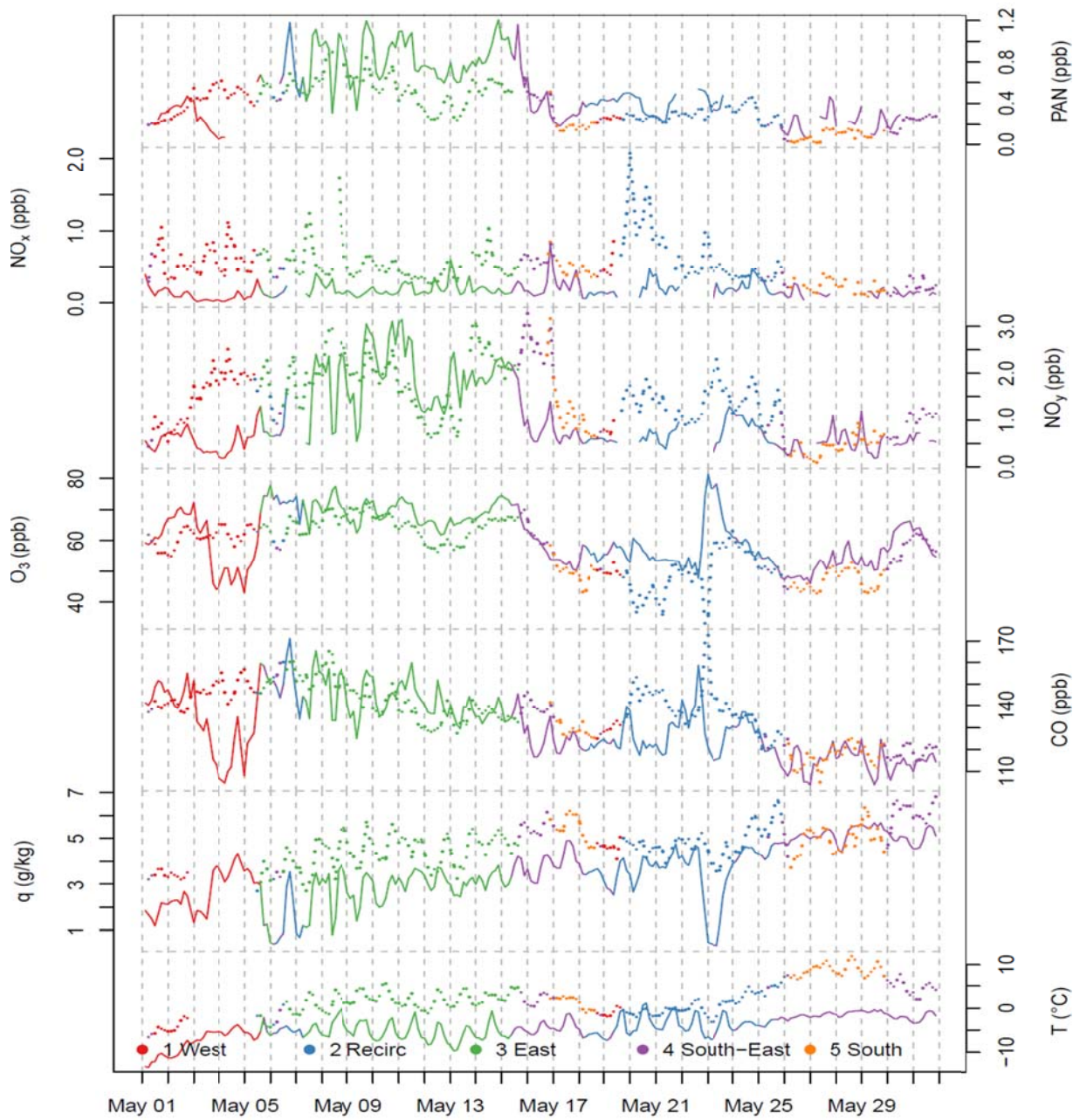
3 Fig. 1. Locations of the sites. Red triangles: locations of the two high Alpine stations
4 Jungfrauoch (JFJ) and Zugspitze Schneefernerhaus (ZSF). Blue circles: The additional
5 elevated PBL sites Chaumont (CHA), Rigi (RIG) and Hohenpeissenberg (HPB).
6



1
 2 Fig. 2. PAN mixing ratios. (a) monthly mean PAN mixing ratios at high mountain sites
 3 Jungfrauoch (JFJ) and Zugspitze Schneefernerhaus (ZSF). Open green circle and
 4 open red triangle: monthly mean values at JFJ for May 2008. Black crosses: campaign
 5 measurements at JFJ during February 2005-August 2006 from (Balzani Lööv et al.,
 6 2008). The grey shaded area shows the measurement range of monthly averages
 7 based on continuous measurements of JFJ and ZSF. JFJ measurements from
 8 2005/2006 were excluded from the shaded area because they did not cover a complete
 9 month. (b) PAN measurements of less elevated sites (Hohenpeissenberg (HPB)) and
 10 PAN measurements during 1987 – 1988 from (Wunderli and Gehrig, 1991) for Swiss
 11 sub-urban (Dübendorf), rural (Lägeren) and low level alpine site (Davos, 1630 m asl).
 12 The grey shaded area shows the measurement range based on all PAN measurements
 13 excluding 2003 which was an exceptional year due to a pronounced European heat
 14 wave.

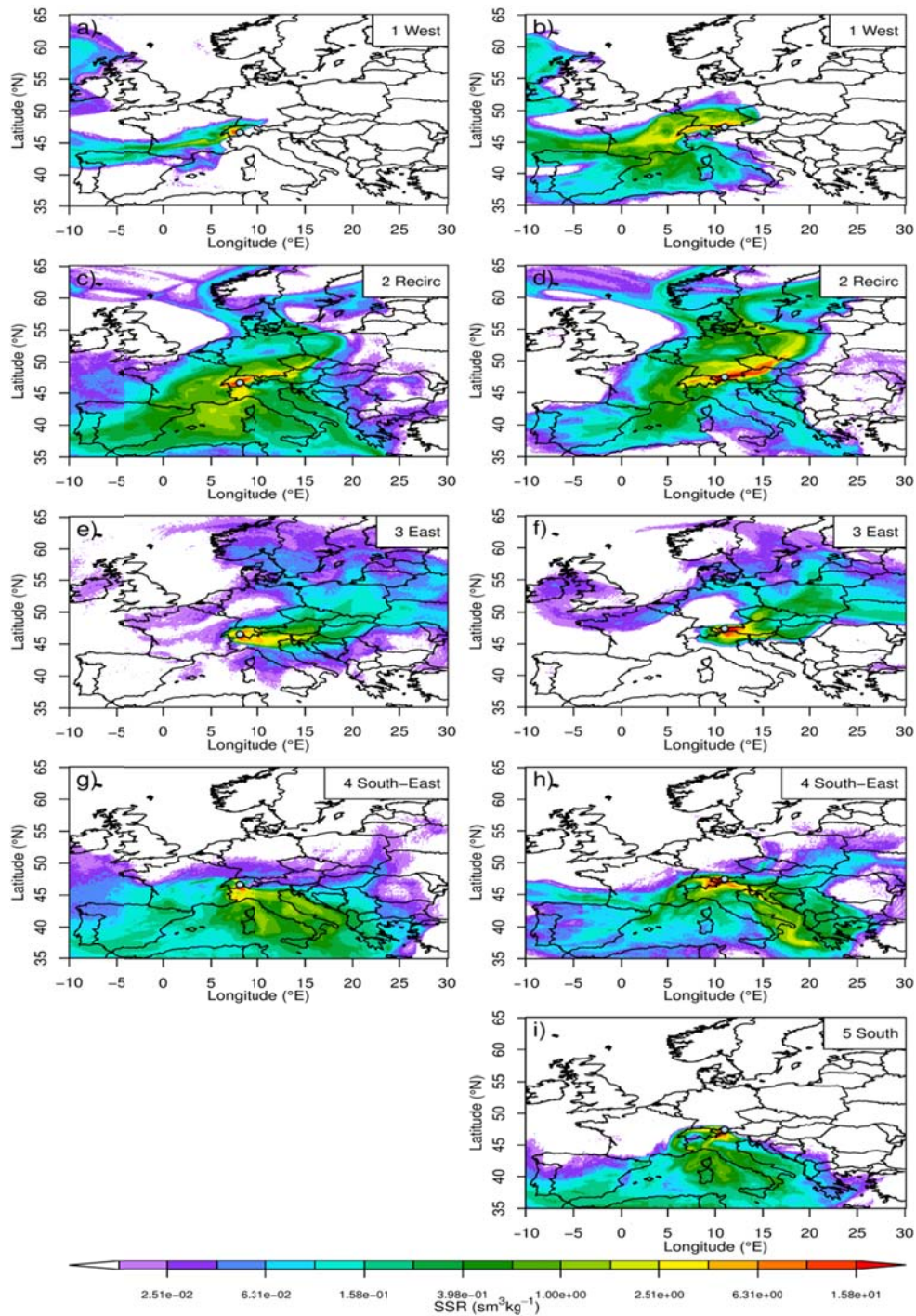
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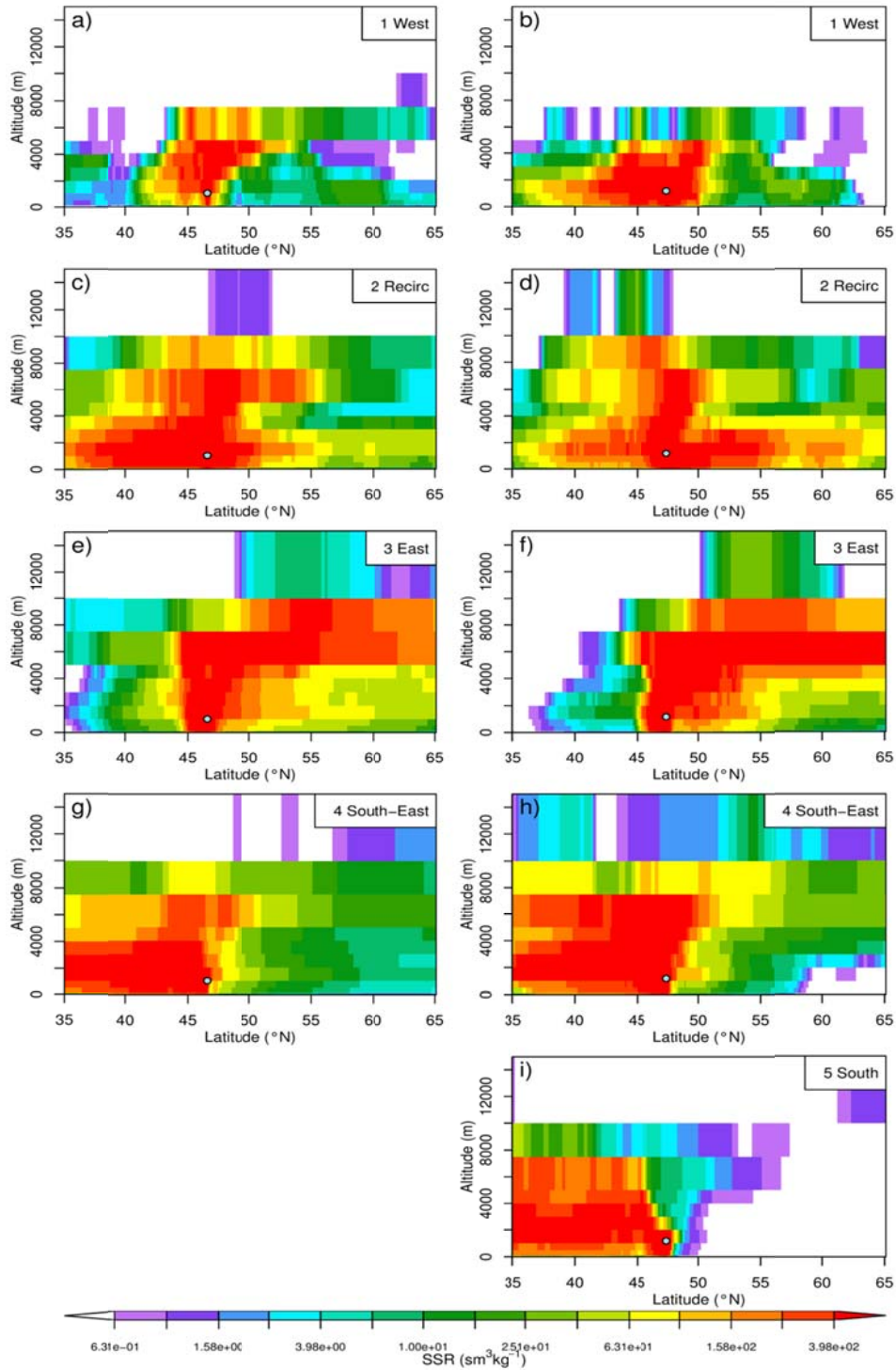


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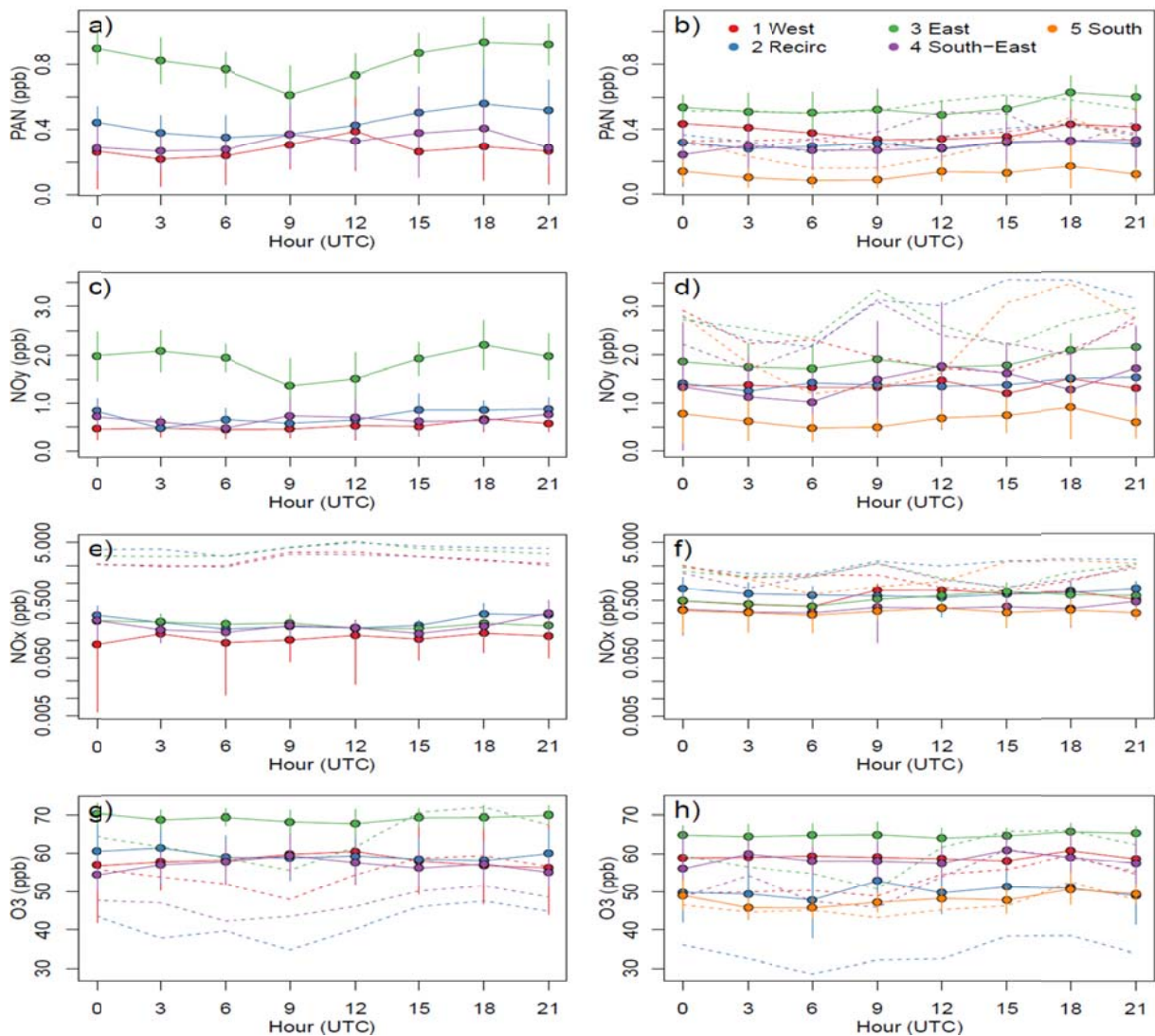
3 Fig. 3. Observed 3-hourly averages of trace gas mixing ratios (ppbv), absolute humidity
4 (g/kg) and temperature (K) at (solid lines) Jungfrauoch and (dotted lines) Zugspitze in
5 May 2008. The colour coding refers to the periods as identified by footprint clustering
6 (see section 4.2.3).



1
 2 Fig. 4. Cluster average surface source receptor relationships (SRRs) for (left: a, c, e, g)
 3 JFJ and (right: b, d, f, h, i) ZSF. Larger SRR indicate a larger sensitivity of the samples
 4 air masses to surface fluxes (emissions or deposition). The sampling locations are given
 5 by a light blue circle.

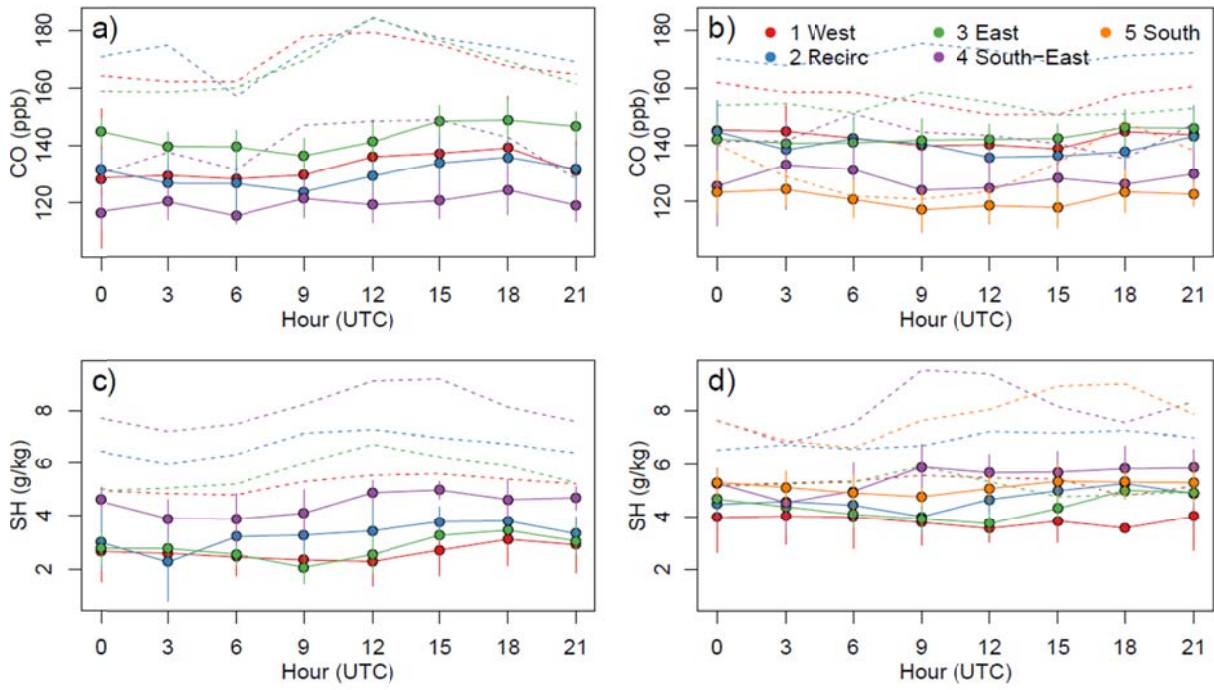


1
 2 Fig. 5. Cluster average latitude-altitude distribution of source receptor relationships
 3 (SRRs) for (left: a, c, e, g) JFJ and (right: b, d, f, h, i) ZSF. The sampling locations are
 4 given by a light blue circle.



1
 2 Fig.6. Average diurnal cycles of (a, b) PAN, (c, d) NO_y, (e, f) NO_x and (g, h) O₃ split by
 3 transport cluster as indicated by the different colours (see definition in b), which
 4 represent the same clusters as in Fig. 3. The solid lines and error bars represent the
 5 high Alpine measurements at (left: a, c, e, g) JFJ and (right: b, d, f, h) ZSF. The dotted
 6 lines give the average diurnal cycle as observed at the reference PBL sites: average of
 7 RIG and CHA for JFJ and HPB for ZSF. The error bars represent expanded uncertainty
 8 (95 % confidence limits) of the 3-hourly cluster means. Note that a logarithmic y-axis
 9 was chosen for NO_x. The time stamp of the 3-hourly aggregates corresponds to the end
 10 of the aggregation interval.

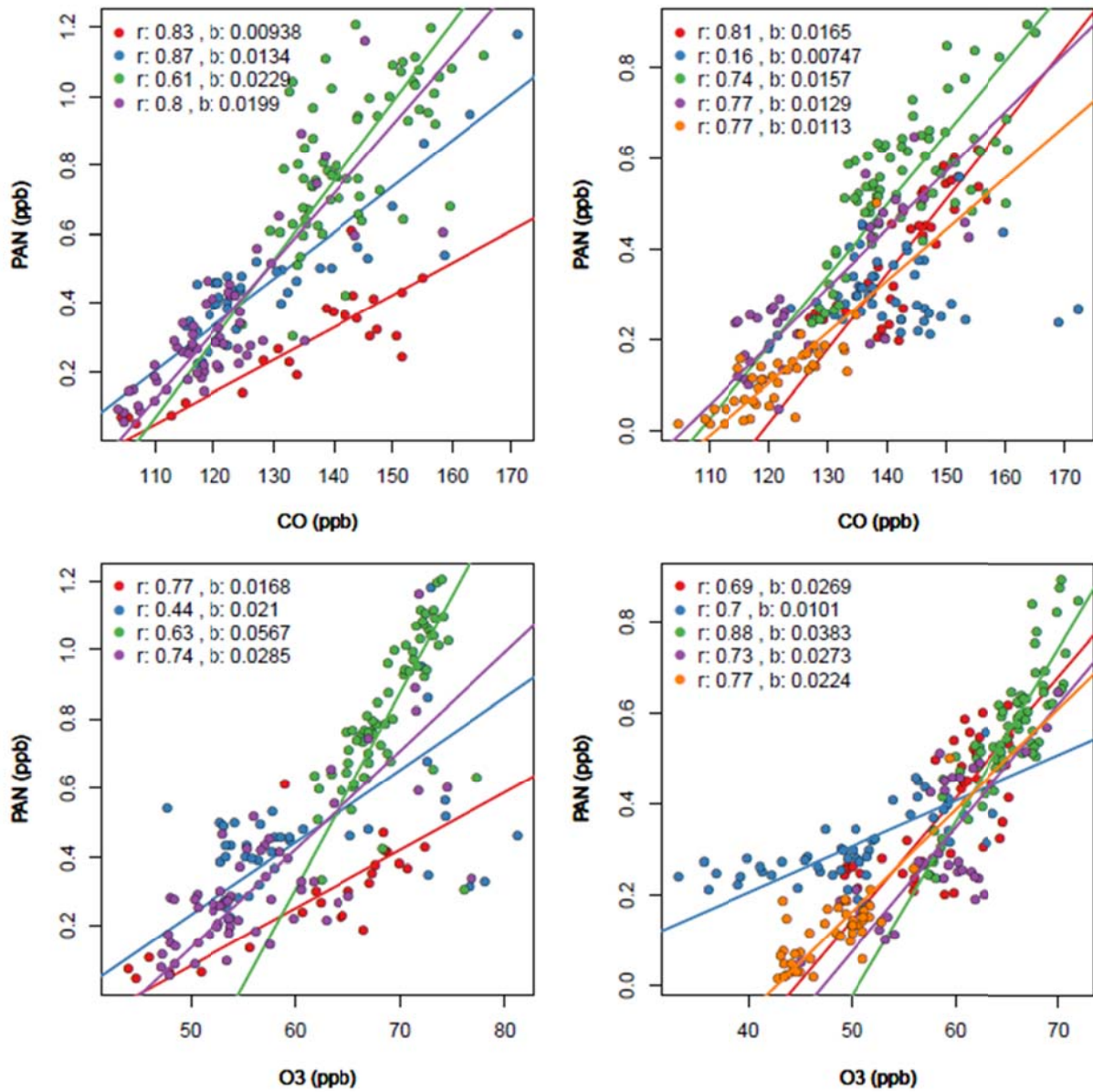
1



2

3 Fig. 7. Same as Fig. 6, but for (a, b) CO, (c, d) specific humidity, (e, f) ambient
4 temperature and (g) global radiation at (left: a, c, e, g) JFJ and (right: b, d, f) ZSF.

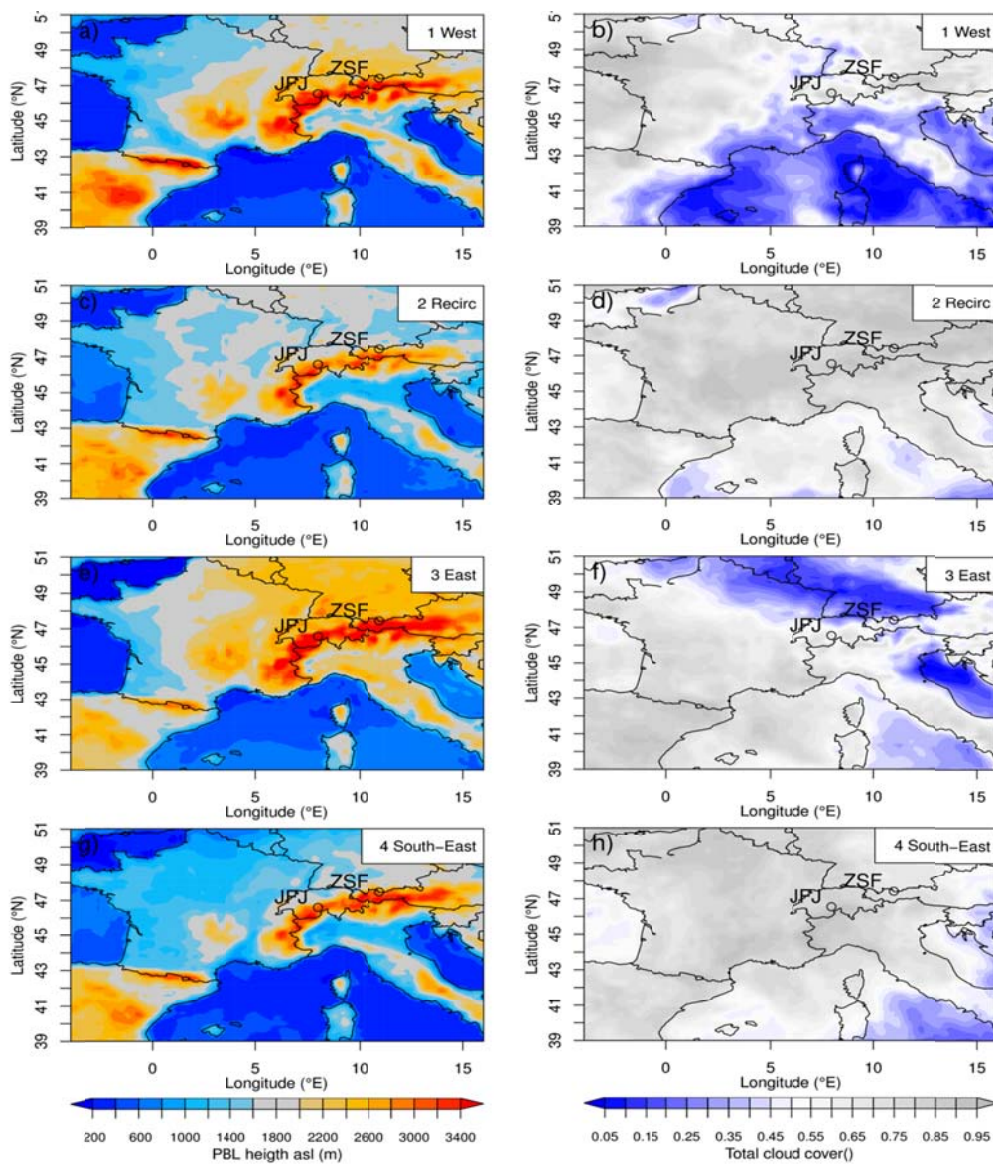
1



2

3 Fig. 8. Scatter plots of observed mole fractions of PAN versus carbon monoxide (top)
4 and PAN versus ozone (bottom) for Jungfraujoch (JFK, left) and Zugspitze (ZSF, right).
5 Regression lines (obtained using weighted total least square regression, see text) are
6 only shown if significant correlations between the trace gases exist. The colours
7 represent the correlations within the individual transport clusters, see Fig. 3 and text).

8



1
 2 Fig. 9. Cluster average for (left: a, c, e, g) afternoon PBL height and (right: b, d, f, h)
 3 daytime total cloud cover fraction for the transport clusters as derived for JFJ. Afternoon
 4 PBL heights were calculated from ECMWF-IFS operational analysis and forecast fields
 5 at 12 and 15 UTC using a critical Richardson number criterion. Day-time total cloud
 6 cover was taken from the same ECMWF fields at (06, 09, 12, and 15 UTC) UTC.

7

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