Seasonal and Diurnal Variation of Formaldehyde and its Meteorological Drivers at the GAW Site Zugspitze

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**ABSTRACT**

Continuous formaldehyde measurements were performed at the high-altitude GAW site Environmental Research Station Schneefernerhaus for more than one year. This unique dataset was analyzed for daily and seasonal variation and for the influence of large-scale synoptic conditions and air-mass origin on the observed concentrations. The average daily course exhibited maxima in the afternoon and minima at night, however differing between seasons. The general strong seasonal variation with average values for winter, spring, summer, and fall of 0.350, 0.529, 0.986, 0.429 ppbv, respectively, could be well explained by secondary production following photochemical activity. The large variability of formaldehyde mixing ratios within the seasons was shown to be influenced by different factors in this complex topography such as mixing of air masses from the planetary boundary layer and the free troposphere, advection of differently aged air from various source regions, and local meteorological conditions. An analysis of the impact of large-scale weather types, cyclonality, and flow directions revealed that the cleanest air masses were advected from westerly directions in particular under cyclonic conditions while southerly cyclonic and northerly/northwesterly anticyclonic conditions led to the highest formaldehyde levels.

**Keywords:** Formaldehyde; Remote site; Trajectories; Large-scale weather types.

**INTRODUCTION**

Formaldehyde (HCHO) is a key substance in atmospheric chemistry, an important radical source in the remote free troposphere (FT), precursor of ozone (O$_3$), and an important indicator of atmospheric photochemical activity. It is also known as a human and animal carcinogen. HCHO is emitted directly by incomplete combustion and evaporation from anthropogenic processes (e.g., road traffic especially diesel exhaust, natural gas, biofuels, biomass burning, chemical and petrochemical industry, industrial production of plastics, solvents and paint, waste water treatment) (Garcia \textit{et al.}, 1992; Grojean \textit{et al.}, 1996; Smidt \textit{et al.}, 2005; Balzani Lööv, 2007; Herndon \textit{et al.}, 2007) as well as from natural and biogenic sources (e.g., living and decaying plants, biomass burning, seawater) (Guo \textit{et al.}, 2009; Luecken \textit{et al.}, 2012).

An HCHO net flux from snowpack during sunlight in arctic climates was reported by Dassau \textit{et al.} (2002), Sumner \textit{et al.} (2002) and Hutterli \textit{et al.} (2004). The largest fraction of atmospheric HCHO results from secondary sources through photochemical production from other directly emitted volatile organic compounds (VOC). Most important secondary formation processes are the oxidation of methane, ethene, propene, and other alkenes such as 1-butene, 1,3-butadiene, and isoprene with additional contribution from much slower oxidation of alkanes and aromatic compounds as well as oxygenated VOCs such as methanol (Arlander \textit{et al.}, 1995; Still \textit{et al.}, 2006; Parrish \textit{et al.}, 2012). Besides a broad range of anthropogenic VOCs that contribute to HCHO production, biogenic sources (e.g., ethene, isoprene) play an important role especially in rural and remote settings during the vegetation period (Duane \textit{et al.}, 2002; Millet \textit{et al.}, 2006; Guo \textit{et al.}, 2009; Luecken \textit{et al.}, 2012).

The apportionment to primary and secondary origin is of interest and has been addressed in several studies (e.g., Solberg \textit{et al.}, 2001; Luecken \textit{et al.}, 2006; 2012; Parrish \textit{et al.}, 2012) reporting that most of the atmospheric HCHO results from photochemical production with large variability.
due to season, climate, and vegetation cover. Nevertheless, in urban areas in winter, direct emissions can contribute up to 50% (Luecken et al., 2012).

HCHO has an average atmospheric lifetime up to two days; however, in the sunlit atmosphere in summer it is reduced to several hours (Lowe and Schmidt, 1983; Seinfeld and Pandis, 1998). Thus, long-range transport cannot be the main contributor to ambient levels at remote sites but rather the frequency of air arriving from the planetary boundary layer (PBL) or in-situ photochemical production from methane, peroxy radicals and other precursors (Solberg et al., 2001; Balzani Lööv et al., 2008). However, precursor compounds can exhibit much larger lifetimes and thus long-range transport of those can add to local or regional compounds can exhibit much larger lifetimes and thus the transport of HCHO or its precursors to the sites (Zanis et al., 1999; Seibert et al., 2000; Balzani Lööv et al., 2008; Legreid et al., 2008). Effects of dilution and loss by deposition that can be particularly important for water-soluble HCHO also play an important role. However, these effects are neglected if only multivariate correlation approaches between different gases are considered (Parrish et al., 2012). Parrish et al. (2012) also stressed the fact that simple correlations between HCHO and other compounds might lead to wrong conclusions about primary or secondary origin. Thus, any correlation with other substances has to be viewed with care and under consideration of confounding factors, especially if primary emissions are deducted from correlations with SO2, NOx, or CO, although HCHO might have been produced photochemically during transport from VOC precursors that were co-emitted during combustion processes with the other substances (Parrish et al., 2012).

For the interpretation of the observed atmospheric composition the origin of air masses is crucial and can be assessed in many different ways. Fleming et al. (2012) summarized different methods applied such as wind sector analysis, trajectory models, and dispersion models and explored advantages and limitations. Trajectory clusters are among the more powerful tools for air-mass history and have been successfully applied to HCHO data from Jungfraujoch by Balzani Lööv et al. (2008).

In this paper, a dataset for more than one year of continuous HCHO measurements at the high-altitude GAW site Zugspitze/Schneefernerhaus is presented and analyzed. First statistical analyses with regard to seasonal distribution are shown and trajectory clusters as well as large-scale weather patterns are examined for meteorological influences on HCHO levels at this background site. Two case studies of the highest values of HCHO in winter and summer, respectively, are presented in the supplement.

**METHODS**

**Experimental Setup**

The remote Environmental Research Station Schneefernerhaus (UFS) is located in the northern limestone Alps at the border of Germany and Austria (47°25’00” North, 10°58’46” East) about 90 km southwest of Munich. It is situated at an altitude of 2650 m a.s.l. on the southern slope of Zugspitze mountain, the highest mountain of Germany, around 300 m below its summit. It is one of the global stations of the Global Atmosphere Watch (GAW) program of the World Meteorological Organization (WMO). The site generally receives FT air but is frequently exposed to PBL air due to thermally induced flow systems especially during summer time (Reiter et al., 1987; Gantner et al., 2003; Pandey Deolal et al., 2014). Thus, air masses with very different origin and history are measured and the site
is particularly suitable for the detection of northern advection (Kaiser et al., 2007). Some influence of surface emissions on trace gas observations have been shown and thus Henne et al. (2010) categorized the site as “weakly influenced”, when analyzing remote air quality sampling sites in Europe. This is due to anthropogenic activities in the direct vicinity of UFS from the adjacent ski and hiking areas on the Schneeferner glacier as well as on the Zugspitze summit and the affiliated tourist services. Detailed site information can be found in the GAW station information system (GAWSIS; http://gaw.empa.ch/gawsis).

Air for analysis of atmospheric formaldehyde (HCHO) was continuously sampled from Dec 6th 2012 to Dec. 15th 2013. The 5 m inlet line (OD ¼”) consisted of Sulfinert© coated stainless steel. The inlet air flow was set to 1 L min⁻¹, the inlet line was heated to an outside temperature of 80°C to prevent build-up of condensate in the line as well as freezing processes on the outside under the extreme conditions especially during the wintertime.

HCHO was measured continuously with an AeroLaser formaldehyde monitor (model AL4021, www.aerolaser.com) using the fluorometric Hantzsch reaction (FHR) described in detail by Junkermann and Burger (2006). It requires the transfer of HCHO from the gas into the liquid phase by stripping HCHO from air in a stripping coil at constant temperature of 10°C to ensure quantitative sampling even at low air pressure present at the UFS. The detection of HCHO employs the fluorescence of 3,5-diacetyl-1,4-dihydrolutidine (DDL) at 510 nm, which is produced from the reaction of aqueous HCHO with an acetylatedone and ammonium acetate solution, with an excitation wavelength of 412 nm (Hak et al., 2005). FHR-based instrumentation have been extensively field-used, compared to other measuring techniques (e.g., spectroscopic, chromatographic), and validated (e.g., Gilpin et al., 1997; Cárdenas et al., 2000; Klemp et al., 2004; Hak et al., 2005; Apel et al., 2008; Wisthaler et al., 2008).

The temporal resolution of the data acquisition was a 10 s mean that in the further analysis was averaged to 30 min mean values. Depending on the time of the gaseous-liquid reactions and the flow-rate settings the delay time of measurement was approximately 4 min (Hak et al., 2005). The determined gas-phase detection limit with a relatively low liquid flow of 0.32 mL min⁻¹ was 24 pptv (3σ of instrumental noise) and close to the determined detection limit of 30 pptv reported by Junkermann and Burger (2006) and of 22 pptv reported by Balzani Lööv (2007). Calibration of the instrument consisted of a liquid and a gas-phase calibration. Absolute calibration of the desired measuring range was performed with aqueous standards (accuracy 0.5%; Bernd Kraft GmbH, Duisburg, Germany) approximately every third week when changing the solutions. Gas-calibration standard was provided by an internal permeation source (Kintek wafer, heated to 45°C) delivering approx. 8 ng min⁻¹ of HCHO that was diluted with 100–150 mL min⁻¹ of zero air. The permeation rate was measured and compared to the liquid standard with every calibration. Daily automatic calibration and zeroing of the instrument were performed with this on-board permeation source and a zero trap at midnight (CET), additional zeroing at noon (CET). The zero-trap consisted of a filter cartridge containing a Hopcalite catalyst (Dräger, Lübeck, Germany) scrubbing HCHO out of ambient air. Further details of the calibration and zeroing procedure are described in Junkermann and Burger (2006).

14.6% of the data were missing due to instrumental failures, power outages, stabilizing times after re-initialization, and rejection by the plausibility control. Another 8.3% of the data were missing due to the twice daily calibration and zeroing procedures, respectively. This resulted in coverage of 77.1% of valid data over the entire measuring period.

Continuous ozone (O₃) measurements were performed by a Thermo Scientific TS49i UV-photometric ozone analyzer with a lower detection limit of 0.5 ppbv, CO with an AeroLaser AL5002 continuous UV-fluorescence monitor with a detection limit of 0.8 ppbv (referred to an integration time of 10 s). NO, NO₂, and NOₓ were measured in parallel with an Econ Physics CRANOXI chemiluminescence detector consisting of a two-channel system to achieve a detection limit of 25 pptv and a Thermo Scientific TS42i trace level chemiluminescence monitor to ensure continuous monitoring of low mixing ratios. NO₃ is measured as NO-equivalent from the output of a photolysis converter. O₃, CO, and NOₓ were sampled with a stainless-steel inlet tube with an inner borosilicate glass tube with a diameter of 10 cm. The inlet flow was highly turbulent with a rate of 500 L min⁻¹. Calibration and quality assurance for these compounds followed the standard operating procedures of the German Environmental Protection Agency (UBA) in accordance with GAW quality standards.

Data for NMHCs were obtained by using automated gas chromatography-flame ionization detection with a Perkin-Elmer system consisting of a Clarus 500 GC equipped with two FIDs and a Turbomatrix 650 Automatic Thermal Desorber unit. Air was sampled through a 5 m heated inlet line (OD 1/8”) of Sulfinert© coated stainless steel with an air flow of 15 mL min⁻¹. Details on the performance of the GC system in an intercomparison experiment can be found in Hoerger et al. (2014).

Trajectories and Data Analysis

Backward trajectories, spatiotemporal pathways of an air parcel, were calculated with HYSPLIT 4 (Hybrid Single Particle Lagrangian Integrated Trajectory Model; version October 2014) (Draxler et al., 1998) from the meteorological model GDAS (Global Data Assimilation System; https://www.ncdc.noaa.gov/data-access/model-data/model-datasets/global-data-assimilation-system-gdas) with a 0.5° resolution. For each day within the entire period eight backward trajectories with a 3-hour interval and a runtime of 96 hours were calculated, starting each day at 02:00 h CET (UTC+1). The selected interval and starting times were necessary to avoid calibration times of the instrument at noon and midnight for which data were missing. Trajectories were started at the coordinates of UFS at an altitude of 1500 m a.g.l. which corresponded well to the average air pressure of 733 hPa at UFS. Each trajectory calculation included
Further analysis of the trajectories was performed with the open-air package (Carslaw and Ropkins, 2012) of the statistical program R (R Core Team, 2014). Trajectory clusters were calculated from all trajectories by using an angle-based distance matrix method applying the \(k\)-medoids algorithm (Sirois and Bottenheim, 1995). The criterion that at least 10% of the trajectories needed to be affiliated with a cluster resulted in a total number of five clusters. In order to derive clearer information on possible background air masses each trajectory was split into two categories: (1) PBL influenced, if the trajectory was running below the mixing layer height over a land mass at least in one time step and (2) FT, if the trajectory always remained above the mixing layer height within the free troposphere. Group comparisons were performed with a two-sided Student’s \(t\)-test, dependencies of two compounds with a linear regression model. All analyses were done in R (R Core Team, 2014).

RESULTS AND DISCUSSION

Seasonal Variability of HCHO Mixing Ratios

The entire time series of HCHO, \(O_3\), CO, NO, and \(NO_2\) from Dec 6\(^{th}\) 2012 to Dec 15\(^{th}\) 2013 are displayed in Fig. 1. A clear annual course of HCHO mixing ratios is revealed with minimal values during wintertime (minimum: 0.05 ppbv on Dec. 9\(^{th}\), 2013, 30 min mean) and maximal values during the summer (maximum: 3.96 ppbv on Aug. 3\(^{rd}\), 2013). However, also in winter, episodes with high HCHO (up to 2.24 ppbv on Jan. 25\(^{th}\), 2013) occurred. These two examples of the winter and the overall maximum are discussed in the case studies in the supplement. The descriptive statistics of the HCHO dataset, also for the different seasons, is given in Table 1. The other gases also show distinct seasonal patterns and other variations throughout the year dependent on emissions, meteorology and photochemistry (Fig. 1) which will be discussed later. The presented HCHO values with 0.429 ppbv (fall mean), 0.350 ppbv (winter mean), 0.529 ppbv (spring mean), and 0.986 ppbv (summer mean) exhibit a clear seasonal pattern. In general, the annual variation of HCHO background is primarily driven by photochemistry that is mainly dependent on solar radiation, producing the highest amounts of secondary HCHO from methane and other precursors during the summer months (Solberg et al., 2001). In addition, biogenic precursors such as isoprene are abundant in much higher amounts in summer and also enhance HCHO levels (Luecken et al., 2012). However, at high-mountain sites such as UFS, which are alternately exposed to aged air masses from the FT and uplifted air from the PBL or the residual layer, synoptic parameters, local meteorological conditions, and topography also play a crucial role. This could also be seen in the monthly maximum that occurred in July and the absolute maximum beginning of August in contrast to June, the month with the highest solar irradiance. During July, the UFS site was also under the influence of long-range transport from arctic North America where a very high activity of boreal forest fires was reported (Trickl et al., 2015). The impact could

Fig. 1. Time series of half-hourly mean values of HCHO, \(O_3\), CO, \(NO_2\), and NO for the period Dec 6th 2012 to Dec 15th 2013. The two highlighted areas mark the winter and the total maximum during the period selected for the case studies.
be seen in elevated CO values. Those air masses have also contributed to the elevated O₃ in July observed at UFS as a result of build-up during transport and possibly contributed to some extent to precursors for HCHO formation.

The HCHO mixing ratios represent a mixture of (diluted) PBL and FT air, thus, the average concentration of the short-lived HCHO depends mainly on the frequency of transport from the PBL (Balzani Lööv, 2007). Birmili et al. (2009) showed that aerosol concentrations at UFS were directly related to mixing layer height that reached a maximum altitude during June with the largest influence of PBL air at the site. During winter the site was mostly exposed to FT air while in summer transport of PBL air occurred frequently according to increasing mixing layer height during afternoons in summer. However, during nighttime in summer, UFS was also exposed to FT air most of the time.

The mean HCHO values of 0.577 ppbv (mean of all data) as well as the seasonal means are in similar ranges as in studies from other remote or rural sites summarized in Smidt et al. (2005), Balzani Lööv (2007), and Khwaja and Narang (2008). However, UFS values are somewhat higher than reported for the high mountain site Jungfraujoch, Switzerland (3580 m a.s.l.), with 0.303 ppbv (mean fall campaign), 0.362 ppbv (mean winter campaign), 0.397 ppbv (mean spring campaign) and 0.505 ppbv (mean summer campaign), respectively (Legreid et al., 2008). This can be explained by a lower altitude of UFS and thus a higher impact of the PBL. The low lying Whiteface Mountain, USA, (1483 m a.s.l.) even exhibits a much higher impact of the PBL (Zhou et al., 2007; Khwaja and Narang, 2008). The HCHO data from six rural sites in Europe, ranging from sea level (Mace Head, Ireland) to 775 m a.s.l. (Donon, France), presented by Solberg et al. (2001) showed similar annual cycles with summer maxima and winter minima with different concentration ranges, mostly above the values at UFS. Data from Mauna Loa (Zhou et al., 1996) were well below the UFS values in the range between 0.149 ppbv (winter seasonal mean) and 0.211 ppbv (summer seasonal mean) which can be explained by the very remote setting on an island in the Pacific without major anthropogenic area sources of a highly populated continent. UFS values were in the range of observations for the respective altitudes and latitudes during flights across Europe reported by Klippel et al. (2011).

In summary, the seasonal HCHO levels found at UFS were in good agreement to other mountain or rural sites as well as to aircraft data from the Northern hemispheric troposphere and show despite temporary influence of the PBL that data can be used for the determination of HCHO background levels.

**Diurnal Variation of HCHO Mixing Ratios**

Fig. 2 shows the diurnal variation of HCHO during the four seasons. For all seasons a clear daily pattern with highest values in the afternoon is revealed. In summer the average maximum reached almost 1.2 ppbv with a nightly minimum still above 0.8 ppbv. The amplitude was highest in summer and lowest in winter where only a slight diurnal profile could be identified. Average HCHO values during winter ranged between 0.3 and 0.4 ppbv during the 24-hour period. This shows on the one hand the photochemical origin of HCHO that increases after sunrise and follows the radiation input. On the other hand, especially in summer, transport of PBL air from the valleys by mountain venting possibly also contributed to the afternoon maximum. This statement is supported by the high standard deviation in the afternoon during summertime indicating higher variability and episodes of high HCHO during that time. This was shown by Birmili et al. (2009) for aerosol concentrations at UFS that were dependent on the mixing layer height with maxima in the afternoon where mountain venting was most abundant. At the very remote site Mauna Loa, Zhou et al. (1996) reported diurnal maxima of up to 0.9 ppbv with upslope winds during summer.

**Photochemical Influence on HCHO and O₃**

A way to assess the secondary origin of substances is a comparison with O₃ that, apart from stratospheric intrusion episodes, is only produced photochemically (Khwaja and Narang 2008). In the seasonal distribution, O₃ also exhibited a maximum abundance in summer and a minimum in winter, and was generally following HCHO in summer (Fig. 1), indicating secondary production of both species. However, differences could be observed during several periods in winter, when low O₃ was accompanied by high HCHO (e.g., 25th Jan. 2013) and vice versa. This phenomenon was investigated in detail in a case study in the supplement. Equally, mixing ratios of both compounds were not concurrent during spring, when O₃ usually exhibits its spring maximum due to the impact of different precursors such as peroxyacetic nitric anhydrides (PAN) that accumulate during winter and peak in early spring at mid and high latitudes, providing NOₓ for O₃ production (Penkett and Brice, 1986; Monks, 2000; Zellweger et al., 2002; Stroud et al., 2003; Pandey Deolal et al., 2014). In addition, biogenic emissions that are contributing an important fraction of HCHO precursors are more abundant in summer than in spring.

Detailed monthly correlations of HCHO with O₃ are

**Table 1.** Descriptive statistics of the HCHO mixing ratios (in ppbv) for the entire period and different seasons (half-hourly mean values).

<table>
<thead>
<tr>
<th>Mixing ratio (ppbv)</th>
<th>Mean</th>
<th>Median</th>
<th>S.D.</th>
<th>Min.</th>
<th>Max.</th>
</tr>
</thead>
<tbody>
<tr>
<td>All data</td>
<td>0.58</td>
<td>0.46</td>
<td>0.39</td>
<td>0.05</td>
<td>3.96</td>
</tr>
<tr>
<td>Winter (DJF)</td>
<td>0.35</td>
<td>0.29</td>
<td>0.23</td>
<td>0.05</td>
<td>2.24</td>
</tr>
<tr>
<td>Spring (MAM)</td>
<td>0.53</td>
<td>0.49</td>
<td>0.22</td>
<td>0.13</td>
<td>1.98</td>
</tr>
<tr>
<td>Summer (JJA)</td>
<td>0.98</td>
<td>0.90</td>
<td>0.46</td>
<td>0.22</td>
<td>3.96</td>
</tr>
<tr>
<td>Fall (SON)</td>
<td>0.43</td>
<td>0.38</td>
<td>0.23</td>
<td>0.09</td>
<td>1.64</td>
</tr>
</tbody>
</table>
Fig. 2. Diurnal variation of the hourly arithmetic mean and standard deviation of HCHO mixing ratios for different seasons (winter = December, January, February; spring = March, April, May; summer = June, July, August; fall = September, October, November).

displayed in Fig. 3. A clear shift in the relationship between the two substances occurred throughout the year. In summer higher HCHO values were accompanied by higher \( \text{O}_3 \) levels indicating common photochemical origins (Balzani Lööv, 2007). Daily HCHO means also showed a significant dependency on daily solar radiation values in June, August, and September (Jun.: \( R^2 = 0.70, p < 0.001 \); Aug.: \( R^2 = 0.38, p < 0.001 \); Sep.: \( R^2 = 0.21, p < 0.05 \)) as well as for the entire dataset (\( R^2 = 0.39, p < 0.001 \)) but not for the rest of the months. This indicates secondary production as the main source of HCHO in summer. No significant relationship between HCHO and \( \text{O}_3 \) was detected for February and March. In the winter months the relationship between HCHO and \( \text{O}_3 \) was inverted resulting from a higher impact of the PBL in winter with a possibly much higher fraction of primarily emitted HCHO from combustion processes. This is supported additionally by a comparison with CO and \( \text{NO}_x \) (see Fig. 1) that correlated well with HCHO in winter but not in summer (not shown here), but secondary production cannot be ruled out completely.

**Synoptic Influence on HCHO Mixing Ratios**

The origin of air masses transported to a receptor site plays a crucial role on HCHO levels. Thus, the dependence of HCHO mixing ratios at UFS on large-scale weather patterns and different trajectory clusters was investigated. Fig. 4 gives an overview of the distribution of HCHO mixing ratios classified into daily large-scale weather types (Hess and Brezowsky, 1952; Werner and Gerstengarbe, 2010) and in Fig. 5 classified into cyclonality and flow direction (following Philipp et al., 2010; Wastl et al., 2013).

The highest HCHO values on average were found under the following weather types in decreasing order (Fig. 4): trough over Western Europe (TRW), northwesterly anticyclonic conditions (NWA), high over Fennoscandia (anticyclonic over Central Europe) (HFA) that occurred quite rarely on only three days, and southerly cyclonic (SZ). Both TRW and SZ belong to the flow direction/cyclonality category southerly cyclonic (SC) that in total exhibited the highest HCHO values (Fig. 5). High HCHO mixing ratios were also observed under northwesterly/northerly anticyclonic conditions (NA), especially under high over Iceland (anticyclonic over Central Europe) (HNA). The lowest HCHO mixing ratios were found under high over Central Europe (HM) and southeasterly anticyclonic conditions (SEA), both very rare weather types with only five and four occurrences, respectively. Frequent weather types with very low HCHO were maritime westerly (WW) and westerly cyclonic (WZ) both in the flow direction/cyclonality category westerly cyclonic (WC). On the one hand cyclonic conditions with rising air may transport HCHO or precursor enriched PBL air to the site, but it is also linked to higher cloudiness with less photochemical potential. On the other hand anticyclonic conditions with subsiding air, but higher solar radiation and thus more potential for photochemical build-up can equally lead to high HCHO values. This shows that high or low HCHO values are not only dependent on the cyclonality, but mainly on the position of the respective high or low and thus on the resulting flow direction and origin of the air mass. The large range of the quantiles of several classes also indicated that other influences such as frequency of injection of PBL air, season, and local or regional factors play an important role and can interfere with the large-scale synoptic patterns.
Fig. 3. Monthly linear regressions of half-hourly mean mixing ratios of HCHO and O₃. Coefficient of determination $R^2$ and slope $a$ are given for each plot.

Fig. 4. Boxplots of HCHO mixing ratios categorized into daily weather types (after Hess and Brezowsky, 1952; Werner and Gerstengarbe, 2010). The boxplots are ordered by the respective HCHO arithmetic mean (not displayed); the width of the boxplots indicates the number of occurrences. The markers indicate the minimum and maximum values excluding outliers (lower and upper bonds), 25th- and 75th-percentiles (lower and upper boundaries of boxes), and medians (horizontal lines inside boxes) are given. Abbreviations are listed in Table 2.
**Fig. 5.** Boxplots of HCHO mixing ratios categorized into cyclonality and flow direction (Philipp et al., 2010; Wastl et al., 2013). The boxplots are ordered by the arithmetic mean (not displayed); the width of the boxplots indicates the number of occurrences. The markers indicate the minimum and maximum values excluding outliers (lower and upper bounds), 25th- and 75th-percentiles (lower and upper boundaries of boxes), and medians (horizontal lines inside boxes) are given. Abbreviations are listed in Table 2.

**Table 2.** Daily weather types of Hess and Brezowsky (1952) classified after cyclonality and flow direction. CE is the abbreviation for Central Europe, FS for Fennoscandia (after Wastl et al., 2013).

<table>
<thead>
<tr>
<th>Flow direction</th>
<th>Cyclonality</th>
<th>Abbreviation</th>
<th>Original definition</th>
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<tr>
<td>Northeasterly, Easterly</td>
<td>Anticyclonic</td>
<td>EA</td>
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<td>Southerly</td>
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HCHO Mixing Ratios by Back-Trajectory Clusters

Fig. 6 illustrates five calculated trajectory clusters with main directions from west (W), northwest (NW), northeast (NE), southwest (SW), and southeast (SE). Fig. 7 gives an overview of chemical and meteorological properties of air masses in the five clusters, also classifying whether the air mass was in contact with the European boundary layer (PBL) or not (FT). In almost all cases mixing ratios were significantly higher ($p < 0.01$) when trajectories passed through the European PBL with the exception of lower $O_3$ in the PBL of cluster NW. No significant differences were observed for $O_3$ in clusters W and NE, CO in cluster NE, and NOx in clusters NE, SW, and SE. Highest HCHO (mean: 0.75 ppbv; PBL influence: 0.83 ppbv; FT: 0.59 ppbv), $O_3$ (mean: 51.6 ppbv), CO (140.6 ppbv), and NOx (0.58 ppbv) mixing ratios were found in cluster NE followed by cluster SW for HCHO (0.65 ppbv; PBL influence: 0.72 ppbv; FT: 0.50 ppbv) and $O_3$ (49.0 ppbv), but not for CO (123.6 ppbv) and NOx (0.20 ppbv) that exhibited quite low values compared to the other clusters. The three shorter clusters NE, SW and SE had the lowest frequencies with 317 (10.5%), 507 (16.8%), and 361 (12.0%) trajectories assigned to the cluster, respectively, but the highest frequencies of contact with the European PBL with 63%, 65%, and 70% of all trajectories, respectively. The more frequent clusters W and NW with 1080 (35.8%) and 750 (24.9%) trajectories only had contact with the European PBL in 40% and 35% of the cases, respectively. This is also reflected in the low values of HCHO and the other gases, which can be explained by long-range transport from rather maritime and FT air masses to the receptor site. The other trajectory categories (NE, SW, SE) stayed longer over the European continent and also mixed more frequently with the PBL leading to higher values of HCHO and other pollutants. Especially relative humidity of the air masses, to a smaller extent air temperature (not significant for SW and SE), clearly distinguishes PBL and FT air masses.

The HCHO mixing ratios of the cluster fractions without PBL influence were substantially higher than modeled background values of 0.29 ppbv for four seasonal campaigns throughout the year for Jungfraujoch, Switzerland, by Balzani Lööv et al. (2008). Cluster W and SE exhibited the lowest FT values with 0.43 and 0.41 ppbv, respectively. The 25th-percentile values of all clusters (range: 0.25–0.32 ppbv) were very close to the calculated value of 0.29 ppbv by Balzani Lööv et al. (2008), but for a more quantitative determination of background concentrations, more elaborate methods are needed.

CONCLUSIONS

One-year data of HCHO mixing ratios showed a high variability diurnally and seasonally. In general the observed patterns resemble very well expected courses from secondary production following the solar radiation input and thus...
Fig. 7. Boxplots of mixing ratios of HCHO, O₃, CO, and NOₓ as well as air temperature and relative humidity for the five trajectory clusters of Fig. 6 for the entire period. The clusters are also differentiated if the air mass was in contact with the European boundary layer (PBL) or not (FT). The markers indicate the minimum and maximum values excluding outliers (lower and upper bonds), 25th- and 75th-percentiles (lower and upper boundaries of boxes), and medians (horizontal lines inside boxes). Significance levels of the two-sided Student’s t-test between PBL influence and FT are: p < 0.01 (**), p < 0.05 (*), p < 0.1 (*), not significant (n.s.).
photochemical decay of precursor compounds. This could be seen by the diurnal variation with maxima in the afternoon and minima at night. During summer, HCHO build-up in the morning starts earlier than in winter following the lengths of days. The diurnal amplitude is also much larger during summer. The importance of secondary production is supported by significant positive correlations of HCHO with O$_3$ and solar radiation during summer months. In winter, the exact opposite could be observed with negative correlations to ozone and solar radiation; spring and fall do not show any consistent patterns. This indicates that photochemistry had a much lower impact on the observed HCHO levels in winter. Possible explanations could be a larger influence of air masses from the PBL with a higher fraction of primary formaldehyde from combustion processes typical for the winter season, such as wood burning and residential heating, although the frequency of uplift of the mixing layer during winter is reduced (Birmili et al., 2009). Local sources from the skiing area might also contribute to some extent. In comparison to summer these emissions are less mixed in a shallower PBL and transport to the site can lead to high HCHO values as seen in a case study for the winter maximum in January (see supplement). However, during summer months, local effects such as thermally induced mountain venting occur more frequently than in winter.

The results show that large-scale synoptic patterns have a great influence on the observed HCHO mixing ratios. On the one hand, they advect air masses of different age and composition from different sources to the receptor site. On the other hand, they lead to different meteorological conditions creating overcast or sunny conditions leading to in-situ photochemistry or washout by precipitation. The cyclonality also triggers if air subsides or is lifted up with the possibility of injecting PBL air into the FT, e.g., during frontal passages or deep convection. At UFS, the highest HCHO levels were found under southerly cyclonic conditions that uplift polluted PBL air from areas such as the highly-industrialized Po valley in Northern Italy or the adjacent Inn valley in Austria. Other weather patterns leading to high HCHO values were anticyclonic conditions with northerly or easterly flow directions. Thus, cyclonality has to be differentiated additionally by flow direction.

Clustering of trajectories identified five air pathways with different properties advecting air masses to UFS. Air was cleaner when staying above the mixing layer height during the 96 hours for all clusters, regardless of its origin. The cleanest were Atlantic air masses without contact to the European continental PBL with westerly flow direction. Higher HCHO levels were found when air masses travelled slower and stayed longer over the European land mass. The highest HCHO levels were found in the northeasterly and the southwesterly cluster.

This study shows that interpretation of observed HCHO values in particular at high-altitude sites with complex topography is challenging. On the other hand, mountain sites offer the potential to investigate those complex chemical and meteorological interactions and to characterize different air masses and different processes in the atmosphere leading to the observed patterns and locate emissions and origin of the trace gases, e.g., by inverse modeling. Thus, apportionment into different photochemical production and loss mechanisms, into biogenic and anthropogenic, or into primary and secondary origin is needed and requires a modeling approach that can also capture the different influencing factors that are more numerous in mountain areas.

**ACKNOWLEDGMENTS**

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**SUPPLEMENTARY MATERIALS**

Supplementary data associated with this article can be found in the online version at http://www.aaqr.org.

**REFERENCES**


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