Concentration of ozone and its precursors at Arosa and Jungfraujoch and their relations to the regional and hemispheric background

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Concentrations of Ozone and Its Precursors at Arosa and Jungfraujoch and Their Relations to the Regional and Hemispheric Background

A dissertation submitted to the
Swiss Federal Institute of Technology Zürich
for the degree of
Doctor of Natural Sciences

presented by

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Abstract

Today the study on regional and global transport of ozone and its precursors is a hot topic in atmospheric chemistry, mainly because ozone in the free troposphere acts as a strong greenhouse gas. This study focuses on the transport of ozone and its precursors under different weather conditions in the Swiss Alps. Trace gas concentrations are investigated considering three kinds of transport processes, the thermal circulation, the frontal passage and the free tropospheric transport. The “local” contribution and regional background (including the contribution of European emission and hemispheric background) at two sites are quantified and compared for Arosa (2010 m asl) and Jungfraujoch (3580 m asl).

In this study measurements of volatile hydrocarbons have been performed by an automated analyzer (AirmoVOC HC1010) at Arosa for more than one year (2001-2002). These measurements have been subsequently compared with simultaneous hydrocarbon measurements at the high alpine station Jungfraujoch. The basic features of the seasonal variations of the hydrocarbon concentrations at Arosa and Jungfraujoch can be explained by the different reactivities of the individual hydrocarbons in the troposphere (i.e. the oxidation by hydroxy radicals). However the background at Jungfraujoch is much cleaner because it is more frequently exposed to the free troposphere. The diurnal variations of hydrocarbon concentrations at both sites show the influence of the thermal circulation in the closest valleys, determined by the locations of the measurement stations. The contributions of the closest sources at both sites are compared to hydrocarbon measurements at a station in the centre of Zürich. The main source of the closest valleys contribution is road traffic emissions at Arosa while the contributions of the solvent usage and gasoline evaporation are also found important at Jungfraujoch.

Meteorological processes have a strong influence on trace gas concentrations at the Alpine sites. The influences of frontal passages and temperature inversions over the Swiss plateau at Arosa and Jungfraujoch are studied. During the synoptic lifting events (frontal passages), the polluted and aged air (compared with the air from thermal lifting) at Jungfraujoch and Arosa are possibly transported from the same large source region, in contrast to the “local” thermal lifting events. The concentrations of ozone and its precursors at Jungfraujoch and Arosa over the temperature inversion layer in winter show the influence of “leaks” of the temperature inversion, transporting primary air pollutants from the densely populated area of the Swiss Plateau. The correlations between ozone concentrations and European residence times of the air parcels in winter suggest ozone production from the “leaked” ozone precursors.

The concentration ratios of two hydrocarbons of different reactivity are determined by the transport processes to Jungfraujoch. The most aged air masses are found in the free tropospheric air primarily when advected by the intercontinental transport. This is the first time that the hydrocarbon transformations during the intercontinental transport are documented by
measurements at a top alpine station. The mean concentration of OH radicals during the transatlantic transport in winter is estimated to be about $5.1 \times 10^5$ cm$^{-3}$.

Trajectories are commonly used tools to study the source-receptor relationship in the atmosphere. However, they have difficulties to describe the transport over the complex topography. Two mesoscale trajectories, ECMWF (European Center for Medium-range Weather Forecast) and aLMo (Alpine Model) are compared. aLMo trajectories based on the forecast wind field are found not more accurate than ECMWF trajectories based on the reanalysis wind field in the detection of the boundary layer influence at Jungfraujoch, though the resolution of aLMo trajectories is higher. However, the relationship between the forecast aLMo trajectories and northerly advection can be used for the detection of frontal passages.

Regional and global models are most suitable for studies of the source to receptor relationship of trace gases at remote sites. A box model and two global chemical transport models (CTMs) are compared to the measurements at Arosa and Jungfraujoch, individually, aiming to compare the methods for studying the regional and global transport. However, in constraint of the resolutions, models are not able to reproduce very well the complex air flow over the alpine region.

The trajectory chemical box model is developed based on ECMWF trajectories and EMEP emissions. The box model simulation gives reasonable concentrations of ozone and its precursors at Arosa in summer. Especially some high concentrations of ozone can be explained by the photochemical formation during transport processes. The simulation result gives evidence that a relation between ozone concentrations and residence times over Europe exists, which can be used for the estimation of European contributions to the remote sites, like Arosa under suitable fair weather conditions.

Simulations of two CTMs, GEOS-CHEM and MOZART are compared to the measurements at Jungfraujoch. The outputs of these numerical simulations were provided by I. Bey (EPFL, Switzerland) and M. Schultz (MPI, Hamburg Germany). Both CTMs well reproduce the seasonal variations of ozone at Jungfraujoch. The use of the wind field with lower horizontal resolution in GEOS-CHEM possibly leads to somehow smaller standard deviations than in MOZART. The point-by-point comparison with the annual measurements at Jungfraujoch shows that the performances of them are statistically not much different. The ozone concentrations are more accurately predicted by MOZART in winter than in summer, suggesting that the boundary layer influence is more difficult to be described than the free tropospheric transport at the remote site Jungfraujoch.
Zusammenfassung


Das Verhältnis der Konzentrationen zwei verschiedener Kohlenwasserstoffe unterschiedlicher Reaktivität hängt von den atmosphärenchemischen und den meteorologischen Prozessen, die den Transport der Luftspurenstoffe zum Jungfraujoch bestimmen ab. Die am meisten gealterten Luftmassen findet man beim Interkontinental-Transport in der freien Troposphäre. In dieser Arbeit werden das erste Mal anhand von Kohlenwasserstoffkonzentrationen von einem hochalpinen Standort die chemischen Prozesse während des interkontinentalen Transportes untersucht. Die Konzentration der OH Radikale während des transatlantischen Transport im Winter wird auf $5.0 \times 10^5 \, \text{cm}^{-3}$ ungefähr geschätzt.


1. Introduction

Ozone (O$_3$) changes in the atmosphere have greatly attracted attention of atmospheric scientists in the last century. Both the increase of ozone in the troposphere and the decrease of ozone in the stratosphere are related to human activities and have a detrimental impact on human beings and the biosphere. Tropospheric ozone increase results from the enhanced anthropogenic emission of volatile organic compounds (VOC) and nitrogen oxides (NO$_x$). Surface ozone concentrations at the alpine site Arosa (Switzerland) and other European rural and remote sites increased by more than a factor of two from the 1950s to the early 1990s (Staehelin et al., 1994). Most of European countries have taken measures to reduce the emission of ozone precursors NO$_x$ and non-methane volatile organic compounds (NMVOC) since the beginning of 1990s in order to mitigate the ozone impact. The emissions of NO$_x$ and NMVOC were substantially reduced in Europe (see Fig. 1-1). However, no clear downward tendency in tropospheric ozone was found in the 1990s (Brönnimann et al., 2002; Monks et al., 2000). Only the peak ozone concentrations in the suburban and rural area showed a decrease (Weber et al., 2002; Scheel et al., 2000; Brönnimann et al., 2002; NABEL, 2002). However, urban ozone maxima remained constant, which is thought to be caused by the decrease of the ozone titration balancing the reduced in-situ ozone production (Weber and Nyffeler, 2002). It was thought that the large scale ozone background becomes more and more important (Wild et al., 2002; Stohl et al., 2001). The steady emissions from the USA and the continual increase of Asian emissions could lead to higher northern hemispheric ozone background (Naja et al., 2003).

Recently Pochanart et al. (2001) compared surface ozone measurements at Arosa with the residence times of the air parcels over Europe as calculated from trajectory analysis. For the summer months, May to August, they found a positive correlation between European residence times and ozone concentrations at Arosa, attributed to photochemical ozone formation from primary air pollutant emissions of Europe. Although the trajectory approach provides a valuable way to learn more about the regional background and the northern hemispheric background (Naja et al., 2002; Pochanart et al., 2003), the method suffers from the uncertainties of weather condition influences (Campana, 2003). Zellweger et al. (2002) have studied the concentrations of reactive nitrogens (NO$_y$ = NO$_x$ + HNO$_3$ + HONO + HNO$_4$ +...) under different meteorological conditions at the measurement station Jungfraujoch and provided valuable meteorological filters for the mountain sites for the discrimination between “undisturbed free troposphere” and “disturbed free troposphere”. However, the so-called injection layer between the boundary layer and free troposphere put the application of this classification at other alpine sites in question (Prévôt et al., 2000).
The layer above the planetary boundary layer is called free troposphere. It still contains substantial amounts of pollutants emitted from the surface, which is indicated for example by the inert hydrocarbons in the aircraft measurements (Penkett et al, 1993; Reeve et al, 2002). In particular, the intercontinental transport plays an important role in the re-distribution of ozone and carbon monoxide (CO) over the northern hemisphere (Stohl et al., 2001; Li et al., 2002).

---

**Fig. 1-1.** NO\textsubscript{x} and NMVOC emissions of Switzerland, the European Union (EU) and the USA, obtained by the emission models of the EMEP (Co-operative Programme for Monitoring and Evaluation of the Long-Range Transmission of Air Pollutants in Europe), MSC-E (Meteorological Synthesizing Centre – East) (http://www.emep.int). NO\textsubscript{x} (NO+NO\textsubscript{2}) emission is calculated in the mass of NO\textsubscript{2}.

In this work, the concentrations of trace gases at Arosa and Jungfraujoch in 2001 – 2002 are investigated and their behaviors are analyzed at both sites with respect to the local, synoptic (frontal) and hemispheric scales. The problems addressed are as follows:

1. What are the differences between the local emissions and the regional backgrounds at Jungfraujoch and Arosa?
2. How can one study the contribution of European emission and hemispheric background with the trajectories at the high mountainous region?
1. INTRODUCTION

(3) How free is the lower free troposphere at the high mountain sites, Jungfraujoch and Arosa, from the European continental boundary layer outflow?

The contribution of European emissions are studied by trajectories and modeling. Two kinds of widely used trajectories, aLMo (Alpine Models) and ECMWF (European Center for Medium-range Weather Forecast) trajectories are used and compared for different synoptic weather types and their availabilities to describe the transport are analyzed statistically based on the trace gas concentrations at Jungfraujoch. In the past the meteorological influences on trace gas behaviors at the high mountainous area were studied focusing on aerosol and reactive nitrogen (Ingold et al., 1999; Zellweger et al., 2002). In this study, the investigation on meteorological influences is extended to carbon monoxide (CO) and volatile hydrocarbons. A photochemical trajectory box model is developed to simulate the regional background of trace gas concentrations and to assist the interpretation of special events at Arosa. However, the hemispheric background variation has to be considered at the remote sites, for example, the intercontinental transport of CO (Pochanart et al., 2003). The source-receptor relationship in the remote sites could only be well identified and quantified by global models for most of species (Tilme et al., 2000). At the end, the outputs of two widely used global models, GEOS-CHEM (GEOS-1 and GEOS-STRAT) and MOZART, which were provided by Isabella Bey (EPFL) and Martin Schultz (MPI), are compared with the ozone concentrations measured at Jungfraujoch. The aspects of the global modeling at a remote mountain site are discussed.
2. Theoretical background: tropospheric ozone and its precursors at remote sites

Concentrations of primary and secondary air pollutants at remote sites are determined by their emissions, photochemistry, advection and dilution during transport from the source to the receptor site. Furthermore, the exchange between the stratosphere and troposphere needs to be considered as well. All these processes depend on the dynamic field in the troposphere. Although stratospheric intrusion occasionally leads to higher ozone concentrations at high mountain sites like Jungfraujoch (Stohl et al., 2000), the anthropogenic emission, either via the long range transport or from local/regional sources, determines the seasonal, diurnal variation and the long term trend of ozone concentrations (Zanis et al., 2000; Pacyna et al., 1991; Weber et al., 2002).

2.1 Photochemistry in the remote troposphere

2.1.1 Overview

The photochemical formation of ozone in the troposphere is initialized by the photolysis of NO$_2$ (R1 and R2). In addition, the reaction between O$_3$ and NO produces NO$_2$ (R3). The balance between the three species by reactions R1-R3 is called the photostationary state. The reactions between NO$_x$ (NO$_x$: NO+NO$_2$) and O$_3$ are very fast. The photostationary state can be reached within 5 minutes in the sunlight (Atkinson et al., 1997).

The photostationary state in the troposphere:

\[ \text{NO}_2 + h\nu (\lambda < 424 nm) \rightarrow \text{NO} + O( ^3P) \]  
\[ \text{O}_2 + O(^3P) + M \rightarrow \text{O}_3 + M \]  
\[ \text{O}_3 + \text{NO} \rightarrow \text{O}_2 + \text{NO}_2 \]

Hydrocarbons are also important ozone precursors in the troposphere (for a more comprehensive overview over the photochemistry of volatile organic compounds in the troposphere see e.g. Seinfeld and Pandis, 1998). The oxidation of hydrocarbons promotes the formation of ozone, through the reproduction of NO$_2$ (R6 and R7). The hydroxy radicals are produced primarily by photolysis of ozone by short wavelength solar radiation in the presence of water vapor (R8 and R9). The oxidation of hydrocarbons by OH produces peroxy radicals, RO$_2$ and HO$_2$ (R4 and R5). These radicals yield NO$_2$ in the reactions with NO. Although CO’s oxidation (R5) contributes to the formation of NO$_2$, the oxidation rate is much lower than those of hydrocarbons. In the polluted urban areas, the formation of O$_3$ is usually hydrocarbon limited.
2. THEORETICAL BACKGROUND

NOx is consumed faster during the transport of the city plumes and the formation of O3 becomes NOx limited in the rural area (Sillman, 1991).

**NO2 reformation through hydrocarbon oxidation:**

\[
\begin{align*}
R^\cdot + OH + M &\rightarrow RO^\cdot + H_2O & \quad (R4) \\
CO + OH + M &\rightarrow HO_2 + CO_2 & \quad (R5) \\
RO_2^\cdot + NO &\rightarrow RO + NO_2 & \quad (R6) \\
HO_2 + NO &\rightarrow OH + NO_2 & \quad (R7) \\
O_3 + h\nu(\lambda < 315 nm) &\rightarrow O_2 + O(^{1}D) & \quad (R8) \\
O(^{1}D) + H_2O &\rightarrow 2OH & \quad (R9)
\end{align*}
\]

In the remote troposphere, Peroxyacetyl nitrate (PAN), as well as the compounds having similar structure, plays an important role for ozone formation. PAN is produced in the oxidation process of aldehydes (R10 and R11), which originate from the oxidation of hydrocarbons (R10) or direct anthropogenic and biogenic emissions. The reversible reaction of PAN (R12) depends on the ambient temperature. Low temperature is favorable for PAN’s formation, which leads to maximum PAN concentrations in spring and minimum concentrations in summer (Tanimoto et al., 2002; Penkett and Brice, 1986). PAN’s decomposition (R12) helps to maintain NOx concentrations and O3 production in the free troposphere. On the other hand, the formation of PAN in the lower troposphere decreases the NO2 concentrations and the production rate of ozone.

**Redistribution of NOx:**

\[
\begin{align*}
RO + O_2 &\rightarrow R'CHO + HO_2 & \quad (R10) \\
R'CHO + OH + O_2 &\rightarrow H_2O + R'CO_3 & \quad (R11) \\
R'CO_3 + NO_2 &\rightarrow PAN & \quad (R12) \\
R'CO_3 + NO &\rightarrow R'O_2 + NO_2 + CO_2 & \quad (R13)
\end{align*}
\]

The effect of PAN can also be thought of as the redistribution of NOx by hydrocarbon oxidation. The above three processes in the free troposphere are sketched out in Fig. 2-1.

![Fig. 2-1. Photochemistry in the free troposphere, composed of three important processes, described in the text. The destruction of RCO3 is through R13, which is not shown in this figure.](image-url)
2. THEORETICAL BACKGROUND

On the global scale, sensitivity simulations without the chemistry of NMHCs (non-methane hydrocarbons) indicated a slightly smaller ozone concentration (<15%) and higher global mean OH concentration (20%) in the remote troposphere (Wang et al., 1998). Without the redistribution of NOx through formation of PAN, NOx concentrations would be 30% lower in the remote lower troposphere (over the sea), but 70% higher in the continental lower troposphere and 40% higher in the upper troposphere. The increase of NOx in the upper troposphere is driven by the deep convection (Wang et al., 1998).

HNO3 was also found to be an important NOx reservoir in the tropical free troposphere (Schultz et al., 2000). HNO3 is formed by the reaction between OH and NO2, which is the most important sink of NOx in hydrocarbon limited areas. Normally HNO3 can be efficiently removed in the boundary layer by wet and dry deposition. However the fast transport during deep convective events in the tropics can transport large amounts of HNO3 to the free troposphere and the reaction rates of photolysis and oxidation of HNO3 are higher than those of PAN. Thus HNO3 becomes the primary contributor to NOx in tropical deep convective events.

2.1.2 Net ozone production in the remote troposphere

In the remote free troposphere, where NOx concentration is low, ozone production rate is mainly determined by reactions R6 and R7. The loss of ozone is through reaction R8 and the reactions with peroxy and hydroxy radicals R14 and R15 as follows:

\[ O_3 + HO_2 \rightarrow OH + 2O_2 \]  
\[ O_3 + OH \rightarrow HO_2 + O_2 \]

The production and loss rate of ozone (PO3 and LO3) is calculated by the equations:

\[ \text{PO}_3 = k_x[H_2O] + k_7[RO_2][NO], \]  
\[ \text{LO}_3 = f_j(O^1D)[O_3] + k_{13}[HO_2][O_3] + k_{14}[OH][O_3]. \]  

The parameter \( f_j \) is the fraction of O1D atoms which react with water vapor to form OH rather than are deactivated by collision with the inert molecules (N2 and O2). NOx promotes the ozone production by the reactions R6 and R7, but the reaction between NOx and radicals removes the radicals in the free troposphere. Overall, ozone change is a complicated process, which is related to the concentrations of HOx, ozone itself and NOx, with NOx concentrations determining the production or loss of ozone in the free troposphere.

Using advanced instrumentation for HOx measurements, the ozone production in the upper free troposphere has been studied in depth (e.g. Zanis et al., 1999). Figure 2-2, obtained during the SUCCESS campaign (Jaeglè, et al., 1998), shows the dependence of net ozone production on NOx in the upper free troposphere. Ozone production increased with the increase in NOx concentration (NOx-limited regime) up to a maximum at the NOx concentration of about 700 ppt (NOx-saturated regime). The Harvard 0-D photochemical model underestimated the HOx concentrations (see the difference between the blue pluses and the red circles in Fig. 2-2) in some cases of insufficient convective injection of aldehyde, acetone, and CH3OOH, as indicated by the sensitivity to acetone (dotted line).
The level of NO$_x$ at which the local production rate of ozone (PO$_3$) balances the loss rate of ozone (LO$_3$) is called the critical NO$_x$ concentration for ozone production in the free troposphere. In the SUCCESS campaign, the critical NO$_x$ concentration was estimated as 10 ppt (see Fig. 2-2). The critical NO levels at Jungfraujoch were found to vary from 10 ppt in January to 20 ppt in March and 25 ppt in July when ozone concentrations are around 50 ppb deduced from the measurements of NO$_x$ and HO$_x$ (Zanis et al., 2000; Carpenter et al., 2000). Zanis et al. (2000) also simulated the in-situ photochemistry for spring 1998 and found that the net ozone production rate in the clean free troposphere was about 0.09 ppb/h.

![Fig. 2-2. Net ozone production (24 hour average) as a function of NO$_x$ above 8 km during the SUCCESS aircraft measurements in April-May, 1996: comparison between steady state point model calculations (blue pluses) and observations (red circles). The three curves show model calculations for average conditions during SUCCESS at an altitude of 11 km, assuming different levels of HO$_x$ sources. The blue dashed line assumes the peroxides and formaldehyde to be in steady state, while the red solid line assumes a convective source of peroxides and formaldehyde. The black dotted line represents the same conditions as the blue dashed line but without production of HO$_x$ from acetone photolysis (Jaeglé et al., 1998).](image)

### 2.2 Characteristics of hydrocarbons

#### 2.2.1 Emissions of anthropogenic hydrocarbons

Anthropogenic non-methane hydrocarbons (HC) originate almost exclusive from ground-based sources. The NMHC emissions from aircrafts are estimated to be negligible for the production of ozone in the free troposphere (Slemr, 2001). The U.K. anthropogenic emission inventory of anthropogenic hydrocarbons includes 8 source categories (Leggett, 1996): (i) petrol exhaust, (ii) petrol evaporation, (iii) diesel exhaust, (iv) solvent usage, (v) gas leakage, (vi) petrol refining and distribution, (vii) industrial and residential waste and (viii) stationary combustion sources. Information about the relative contributions of individual organic com-
pounds to road traffic emissions in Switzerland can be obtained from Gubrist tunnel measurements (Staehelin et al., 1996). Statistical analysis (i.e. principal component analysis with visual inspection) of the NMHC measurements in Zürich and Wallisellen revealed two main sources, on-road traffic emission and gasoline evaporation, which contribute to the total volatile non-methane hydrocarbons (ethane to toluene) by 27% and by 34% respectively (Staehelin et al., 1997). The on-road traffic emission includes two sectors in UK emission inventory, namely petrol exhaust and diesel exhaust while the gasoline evaporation is covered by other two sectors in the UK emission inventory, namely petrol evaporation and petrol refinery and distillation. Table 2-1 gives the source sectors of several hydrocarbons in three main sources (on-road traffic, gasoline evaporation and solvent usage), according to the UK inventory (Legette, 1996). The largest contribution of toluene and xylenes is the solvent usage, while the highly volatile hydrocarbons, especially iso-pentane and n-pentane, are primarily from gasoline evaporation.

**Table 2-1.** Source sectors of anthropogenic hydrocarbons. The contribution percentages are based on the UK anthropogenic emission inventory (Leggett, 1996).

<table>
<thead>
<tr>
<th>Compounds</th>
<th>on-road traffic</th>
<th>gasoline evaporation</th>
<th>solvent usage</th>
<th>Others</th>
</tr>
</thead>
<tbody>
<tr>
<td>iso-butane</td>
<td>18.8</td>
<td>43.1</td>
<td>37.1</td>
<td>1.0</td>
</tr>
<tr>
<td>n-butane</td>
<td>21.2</td>
<td>52.3</td>
<td>24.4</td>
<td>2.1</td>
</tr>
<tr>
<td>iso-pentane</td>
<td>51.8</td>
<td>44.0</td>
<td>2.1</td>
<td>2.1</td>
</tr>
<tr>
<td>n-pentane</td>
<td>34.7</td>
<td>49.0</td>
<td>3.5</td>
<td>12.8</td>
</tr>
<tr>
<td>2-methylpentane</td>
<td>62.7</td>
<td>29.0</td>
<td>6.1</td>
<td>2.2</td>
</tr>
<tr>
<td>3-methylpentane</td>
<td>60.7</td>
<td>27.7</td>
<td>9.0</td>
<td>2.6</td>
</tr>
<tr>
<td>n-hexane</td>
<td>40.3</td>
<td>15.3</td>
<td>42.2</td>
<td>2.2</td>
</tr>
<tr>
<td>Benzene</td>
<td>87.9</td>
<td>9.5</td>
<td>-</td>
<td>2.6</td>
</tr>
<tr>
<td>n-heptane</td>
<td>58.7</td>
<td>16.3</td>
<td>20.8</td>
<td>4.2</td>
</tr>
<tr>
<td>Toluene</td>
<td>58.9</td>
<td>6.1</td>
<td>34.8</td>
<td>0.2</td>
</tr>
<tr>
<td>ethylbenzene</td>
<td>92.9</td>
<td>6.9</td>
<td>-</td>
<td>0.2</td>
</tr>
<tr>
<td>m,p-xylene</td>
<td>60.7</td>
<td>4.3</td>
<td>34.9</td>
<td>&lt;0.05</td>
</tr>
<tr>
<td>o-xylene</td>
<td>55.5</td>
<td>4.1</td>
<td>40.3</td>
<td>&lt;0.05</td>
</tr>
</tbody>
</table>

**2.2.2 Concentration ratios between hydrocarbons**

**2.2.2.1 Photochemical degradation of hydrocarbons induced by OH radicals**

Hydrocarbons in the troposphere are mainly degraded through oxidation by OH (R4). The degradation rate of $X$ is

$$\frac{dX}{dt} = -k_X [OH] Y,$$

(2-4)

where $k_X$ is the reaction constant of the oxidation by OH radicals. Because of different reactivities (Atkinson et al., 1991), the ratios between two hydrocarbons ($X$ and $Y$) have the following relation to the residence time $t$ in the atmosphere after they are released:
The ratios of the concentrations of two hydrocarbons, which have different oxidation rates, can be used to describe the aging of an air mass as long as mixing of air parcels can be ignored and the composition of hydrocarbons is constant upon the emission source. The following relationship between the concentration ratio of two hydrocarbons ($X/Z$) and of another pair of hydrocarbons ($Y/Z$) exists if all the pollutants originate from the same source:

$$\ln(X/Z) = b + \frac{(k_x - k_y)}{(k_y - k_z)} \ln(Y/Z), \quad (2-6)$$

where $b$ is a constant, determined only by the composition of the source. However, the correlation between two hydrocarbon pairs found in field measurements did not agree with equation (2-6) very well (Roberts et al., 1984). The deviation was most probably caused by the dilution in the long range transport (McKeen et al., 1993 and 1996).

### 2.2.2.2 Theoretical explanation of the relation between hydrocarbon concentrations

Further research on the hydrocarbon concentrations included both the effects of dilution and photochemistry (McKeen et al., 1993). The mixing ratios of species $X$ are determined by chemical loss and mixing with an infinite reservoir of background air, if there are no other sources during transport. The concentrations of hydrocarbons during such a transport event can be represented by the following equation:

$$\frac{dX}{dt} = -L_X X - K(X - X^B), \quad (2-7)$$

where $X$ is the mixing ratio of species $X$, $t$ is time, $X^B$ is the prescribed mixing ratio of $X$ in the background air, $L_X$ is the loss frequency of species $X$ by OH oxidation (bimolecular reaction rate constant $k_x[OH]$) and $K$ is a dilution coefficient used to parameterize all the mixing process of species $X$ with the background air. If $K$ and $L_X$ are assumed to be constant, the mixing ratio of $X$ at time $t$ is determined by the following equation:

$$X = \frac{K \cdot X^B}{K + L_X} + \left(\frac{X^0 - K \cdot X^B}{K + L_X}\right)e^{-(K + L_X)t}, \quad (2-8)$$

where $X^0$ is the initial mixing ratio of $X$ upon emission.

Two extreme conditions are considered. Firstly, if $X^B$ and $Y^B$ and $Z^B$ are zero, equation 2-6 is obtained. Secondly, if the species are inert, the hydrocarbon ratios from the model have a relationship determined by the ratios of emission and background:

$$\frac{X}{Z} = \frac{Y}{Z} \cdot \frac{(E^{X/Z} - B^{X/Z})}{(E^{Y/Z} - B^{Y/Z})} + \frac{(E^{X/Z} B^{Y/Z} - E^{Y/Z} B^{X/Z})}{(E^{Y/Z} - B^{Y/Z})}, \quad (2-9)$$

where $E^{i/z}$ and $B^{i/z}$ are the emission ratio and background ratio of species $I$ to species $Z$, respectively. If species $X$ and $Y$ have zero background, the logarithms of two hydrocarbon ratios $X/Z$ and $Y/Z$ will yield a correlation line with a slope of unity. Figure 2-3 shows an
$X/Z$ and $Y/Z$ will yield a correlation line with a slope of unity. Figure 2-3 shows an example from aircraft measurements in PEM-WEST A (McKeen et al., 1996), in which the correlation between $\ln(n\text{-}C_4H_{10}/C_2H_6)$ and $\ln(C_3H_8/C_2H_6)$ falls into the range between two extreme conditions.

Equation 2-9 also suggests a relationship between logarithms of mixing ratios of two hydrocarbons with zero background:

$$\frac{X}{X_0} = \left(\frac{Y}{Y_0}\right)^{K+L_x}. \quad (2-10)$$

This equation suggests that the contribution of dilution ($K$) can be estimated through the correlation between the logarithms of two hydrocarbons if the background concentrations of the species can be neglected.

This concept allows estimation of the dilution constant $K$, the background concentrations of the inert species and the concentration of OH at remote sites (McKeen et al., 1996). Although the ratios of hydrocarbons suffer from different sources and dynamical process, the ratios can be used to obtain information of the oxidation states, to estimate the OH concentrations (Blake et al., 2003) and to explain the seasonal variations of the hydrocarbon concentrations at the sites with simple distribution of sources. (Boudries et al., 1994).

**Fig. 2-3.** Correlation of $\ln(n\text{-}C_4H_{10}/C_2H_6)$ versus $\ln(C_3H_8/C_2H_6)$ in PEM-West A flight measurements over the Pacific Ocean in the vicinity of the Asian continent, in September to October, 1991 (McKeen et al., 1996). The solid line represents the slope for OH oxidation, the dotted line the slope for dilution of the inert species (see text).
2. THEORETICAL BACKGROUND

2.2.2.3 An empirical equation and its applications

An empirical relationship (2-11) between the standard deviation of mixing ratios and the lifetime for species in the atmosphere was applied to non-methane hydrocarbons measured in the project NARE in 1993 (Jobson et al., 1999).

\[ \sigma(\ln(X)) = A \tau^{-b} \]  

(2-11)

where \( \sigma(\ln(X)) \) is the standard deviation of the natural logarithm of \( X \)'s concentration, \( \tau \) is the lifetime of \( X \). The deviations of the concentration logarithms have a linear relation to the lifetimes on a logarithmic scale for the hydrocarbon species.

The relationship between the variations of the concentration logarithms and lifetimes of \( X \) is not influenced by the mixing process, contrary to the relationships between two hydrocarbon concentration ratios discussed in Section 2.2.2.2, and provides a valuable method to assess the quality of the hydrocarbon and halocarbon measurements (William et al., 2000). The equation is also applicable to the estimation of OH concentrations (Ehhalt D. H., 1998; William et al., 2000; Karl et al., 2001). The OH concentrations can be estimated by the best fit between the standard deviations of logarithmic concentrations and the atmospheric lifetimes of the species, when photolysis or oxidation by ozone is also important. Figure 2-4 shows how the ambient concentration of OH radicals was obtained from the concentrations of volatile organic compounds measured at the Sonnblick Observatory (3106 m, 47.05°N, 12.3°E) in November 1999 (Karl et al., 2001). It should be noted that the method is only applicable for species, such as alkenes and oxygenated organic compounds, which have other significant degradation mechanisms in addition to OH oxidation. This is because the variations of lifetime with different OH concentrations do not influence the regression coefficients (see Eq. 8-1) in the degradation only through OH oxidation.

The factor \( b \) in equation 2-11 is related to the contributions of both the photochemical degradation and mixing process. When there are various sources, the factor \( b \) approaches zero. If the observed variability is primarily dependent on the degradation, the value of \( b \) approaches unity. In the stratospheric air masses, \( b \) was estimated to be 1.0 for halocarbons (Jobson et al., 1999). In the typical continental background, \( b \) is around 0.5 for oxygenated hydrocarbons (Karl et al., 2001). The strong diurnal variation of the anthropogenic oxygenated hydrocarbons caused by the mixing in the mountainous region led to a smaller \( b \) value of 0.11 (see the blank squares in Fig. 2-4). However, the relation for biogenic hydrocarbons at the same time showed values of \( b \) close to 1.0, which was linked the degradation of the nearby biogenic emission.
Fig. 2-4. (a) Variability versus lifetime of VOCs, measured in Sonnblick Observatory (Karl et al., 2001). The anthropogenic contribution is represented by squares, with open squares for the beginning of November, closed squares for 25-27 November 1999 and closed triangles show the biogenic contribution of 25-30 November and close circles are a subset on 27 November (Numbers 1-8: hexanal, heptanal, octanal, nonanal, methylbutanal, hexanals, ethyl vinyl ketone and methyl vinyl ketone plus methacrolein), (b) The minimum squared 2-norm of the residual as a function of the OH density. The minimum yields the optimal OH-density of \((1.5 \pm 0.5) \times 10^5 \text{ cm}^{-3} \text{ s}^{-1}\).
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2.2.2.4 Photochemical degradation of hydrocarbons induced by Cl radicals

The oxidation by OH was found to be insufficient to explain the hydrocarbon behaviors in the marine boundary layer (Penkett et al., 1993). NO₃ had been thought to be a possible oxidant in the marine boundary layer (Penkett et al., 1993) and polluted urban environment, but the very low reaction rate of NO₃ can not yield a degradation rate comparable to the oxidation by OH. The oxidation of hydrocarbons by chlorine radicals was recently found to be also responsible for the hydrocarbon degradation in the Arctic marine boundary layer, at Alert (Finlayson-Pitts and Pitts Jr., 1997). The rate constants for the reactions of Cl atoms with i-butane and propane are similar and about half of the rate constant for reaction of Cl atoms with n-butane (see Table 2-2). Thus, i-butane and propane decayed at similar rates when Cl atoms were considered as the primary oxidant in the measurements in the arctic troposphere (Fig. 2-5).

![Fig. 2-5. Relative concentrations of propane, n-butane and i-butane in the Arctic troposphere at Alert, Canada, and on an ice floe 150 km north of Alert (Finlayson-Pitts and Pitts Jr., 1997).]

Cl atoms are produced by the reactions between trace gases and sea salt particles. The mechanism of Cl production in the marine boundary layer remains to be elucidated (Wayne, 2003). The concentration of Cl in the marine boundary layer was first estimated by Wingenter et al. (1996) using a sophisticated statistical method based on the OH and Cl oxidations of hydrocarbons and halocarbons. The estimated concentrations of Cl are included in Table 2-2.
Table 2-2. Rate constants of hydrocarbons oxidation by OH, NO$_3$ (Atkinson et al., 1997; 2000) and Cl (Qian et al., 2001) at 298 K, 1 atm and the ambient concentrations of OH, NO$_3$ and Cl

<table>
<thead>
<tr>
<th>Hydrocarbon</th>
<th>OH (cm$^3$·s$^{-1}$)</th>
<th>NO$_3$ (cm$^3$·s$^{-1}$)</th>
<th>Cl (cm$^3$·s$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ethane</td>
<td>2.40 × 10$^{-13}$</td>
<td>&lt; 1× 10$^{-17}$</td>
<td>5.2 × 10$^{-11}$</td>
</tr>
<tr>
<td>Propane</td>
<td>1.10 × 10$^{-12}$</td>
<td>&lt; 7× 10$^{-17}$</td>
<td>1.36 × 10$^{-10}$</td>
</tr>
<tr>
<td>i-butane</td>
<td>2.44 × 10$^{-12}$</td>
<td>-</td>
<td>1.40 × 10$^{-10}$</td>
</tr>
<tr>
<td>n-butane</td>
<td>2.30 × 10$^{-12}$</td>
<td>6.5× 10$^{-17}$</td>
<td>1.91 × 10$^{-10}$</td>
</tr>
<tr>
<td>iso-pentane</td>
<td>3.55 × 10$^{-12}$</td>
<td>-</td>
<td>1.94 × 10$^{-10}$</td>
</tr>
<tr>
<td>n-pentane</td>
<td>4.00 × 10$^{-12}$</td>
<td>8.0× 10$^{-17}$</td>
<td>2.46 × 10$^{-10}$</td>
</tr>
<tr>
<td>n-hexane</td>
<td>5.61 × 10$^{-12}$</td>
<td>-</td>
<td>3.44 × 10$^{-10}$</td>
</tr>
<tr>
<td>Benzene</td>
<td>1.16 × 10$^{-12}$</td>
<td>-</td>
<td>0.04 × 10$^{-10}$</td>
</tr>
<tr>
<td>Toluene</td>
<td>5.64 × 10$^{-12}$</td>
<td>-</td>
<td>0.56 × 10$^{-10}$</td>
</tr>
</tbody>
</table>

Concentrations (cm$^{-3}$)* 1 × 10$^6$ 1 × 10$^8$ 10$^4$$^-$$10^5$

* OH – global mean concentration (Prinn et al., 2001).
NO$_3$ – peak concentration measured at Jungfraujoch (Wayne et al., 1991).
Cl – maximum concentration at Dawn over the Atlantic Ocean in summer 1992 (Wingenter et al., 1996).

2.3 Trace gas concentrations over mountainous areas

2.3.1 Thermal circulation and the synoptic wind system in the alpine mountainous region

Recently several studies concerning the transport processes over the mountainous area have been carried out. In the project VOTALP (Vertical Transport over Alpine Regions), the so called injection layer was found to significantly influence the trace gas distribution over alpine region (Furger et al., 2000). The daytime wind field on a fair day illustrates three layers at the low alpine site, Cadenazzo (400 m a.s.l.): Layer 1 is the well mixed boundary layer below 2000 m; Layer 2 is between 2000 and 3500 m, in which the wind remains in the same direction as over the surface but sometimes rotates to the direction of the synoptic flow; Layer 3 is the free troposphere, depicted by low water vapor and aerosol content. The normal circulation system is strongly related to the synoptic conditions. In addition, the up-slope wind can also reach the crest of the mountain, which cannot be explained by the stability of the atmosphere (Baltensperger et al., 1997). The accepted explanation of the up-slope wind is the thermal heating in the surface layer of the slope, but the exact mechanism is still unclear (Rampanelli et al., 2003). The measurements of aerosol optical depth, water vapor content and total suspended particulate matter (TSP) at Jungfraujoch indicated that the passage of the up-slope wind occurred generally in the late afternoon during the convective days (Ingold et al., 2001; Lugauer et al., 1998). Henne et al. (2003) quantified that air masses of about three times of the valley volume were exported by the up-valley flow under fair weather conditions in the Mesolcina valley in the southern Swiss Alps.

Figure 2-5 shows the scheme of the injection layer during daytime, which is taken from VOTALP II and adjusted to the situations of Arosa (2010 m a.s.l.) and Jungfraujoch (3850 m a.s.l.)
2. THEORETICAL BACKGROUND

a.s.l.). The black arrows indicate the up-slope air flow. In the direction of synoptic wind, the concentrations of primary pollutants increase due to the up-valley transport. The grey arrows show the daytime evolution of the boundary layer, which reaches the highest level in the afternoon, most possibly over the crests of the mountains around Arosa. During the nighttime, the downward transport prevailed. However, the air masses from the upper layer are possibly influenced by the injection, which in the nighttime can also be viewed as the residual layer (Stull et al., 1988). In comparison, Jungfraujoch is at the crest of the Alps and at the top of the injection layer and most of the time in the free troposphere.

![Diagram of air flow over alpine mountains](image)

**Fig. 2-5.** Air flow over alpine mountains found in VOTALP II (1998-2000) and adjusted to the location of Arosa and Jungfraujoch, showing the position of Arosa and Jungfraujoch in relation to the injection layer and the free troposphere (refer to [http://lac.web.psi.ch/LAC_Projects/VOTALP/VOTALP2main.html#VOTALP2_Goals](http://lac.web.psi.ch/LAC_Projects/VOTALP/VOTALP2main.html#VOTALP2_Goals)). The shaded arrow shows the growth of the well-mixed boundary layer.

2.3.2 Dry and wet depositions

Dry and wet depositions are important processes acting as sinks of ozone and other trace gases, like nitrogen oxides and soluble compounds, in the boundary layer. The removal of trace gases at the surface by chemical, physical and biological processes in the absence of precipitation is defined as dry deposition. The dry deposition velocity \( V_d \) is theoretically expressed in dependence of specific characteristics of surfaces and the atmospheric conditions above the surface:

\[
V_d = \frac{1}{R_a + R_l + R_{surf}}, \tag{2-12}
\]

where \( R_a \) is the aerodynamic resistance, which is a function of the turbulence in the surface layer, related to boundary layer stability, wind speed and surface roughness, \( R_l \) is the quasi-laminar boundary laminar layer resistance, partially controlled by molecular diffusion, and \( R_{surf} \) is the combined resistance of all transfer pathways (vegetation, soil and water, ice and snow) which play a role in the uptake of trace gases by the surface. Ganzeveld and Lelieveld (1995) found that deposition of HNO\(_3\) has a stronger dependence on \( R_a \), whereas O\(_3\) and NO\(_x\) depend more on \( R_{surf} \). The nighttime downward wind over mountainous region leads to efficient ozone removal (Broder and Gygax, 1985). The dry deposition of O\(_3\) and NO\(_x\) (NO and
NO$_2$) is very weak compared to HNO$_3$. The NO$_2$ dry deposition velocity is found to be about 2/3 of the ozone dry deposition velocity over the plant covered area (Wesely, 1989).

Dry deposition was found to contribute to 34% of the total reactive N deposition (wet and dry) at Harvard forest in 1990-1996 (Munger et al., 1998). In the process of the removal of N species in the boundary layer, NO$_x$ can be efficiently converted to HNO$_3$ by homogenous and heterogeneous reactions. HNO$_3$ is then efficiently removed by dry and wet deposition. The characteristic time for removal of NO$_x$ oxidation products from the boundary layer by wet and dry deposition is about 1 day in summer (Munger et al., 1998).

### 2.3.3 Long range transport of ozone and its precursors

Ozone formation is a complicated nonlinear process influenced by the meteorological conditions, which involves many reactions and some unknown mechanisms (Wayne, 2002). Although the formation process is nonlinear, the ozone increase during transport in the boundary layer is close to being a linear process (Derwent et al., 1993; 1996), especially when the mixing happens at the top of the mixing layer. A simple statistical model based on linear increase of ozone concentrations has been applied to separate the hemispheric background and the European contribution and also to study the ozone trend in hemispheric background, which gave reasonable results (Pochanart et al., 2001 and Naja et al., 2003). The increase in background ozone concentration in Europe was thought to be related to the hemispheric transport (Stohl et al., 2002).

The intercontinental transport was found to be an important mechanism for distribution of ozone and its precursors in several studies with Chemical Transport Models (CTMs) and Lagrangian particle dispersion models (LPDMs) (Wild and Akimoto, 2001; Stohl et al., 2002; Bey et al., 2001b; Li et al., 2002). The basic intercontinental transport paths have been summarized by Bey and Schulz (2002). Furthermore, long-lived compounds have been used as tracers to show the intercontinental transport (Stohl et al., 2002; Pochanart et al., 2003; Wenig et al., 2002). The CTMs, which can estimate the source and sink budget of species in the global scale, are very suitable tools for the tropospheric chemistry research.
3 Measurements and methodology

3.1 Description of the sites

The locations of the two measurement stations, Arosa and Jungfraujoch in the Swiss Alps are shown in Fig. 3-1.

The Arosa measurement station (2010 m asl, 9.76°E, 46.67°N) is situated on the slope of the Plessur valley, 200 m above the village of Arosa. Chur, the biggest city at the mouth of the valley, is 25 km away from Arosa. The orientation of the Plessur valley changes sharply from E-W to NE-SW between Arosa and Chur, and Arosa is consequently surrounded by mountains of 2500-3000 m asl.

The Jungfraujoch measurement station (3580 m asl, 46.55°N, 7.98°E) is located on a mountain saddle between Jungfrau (4158 m asl) in the west and Moench (4099 m asl) in the east. The northern slope drops down to 2000 m in a horizontal distance of 2-3 km. The closest valley to the south is further away than the valley to the north.

3.2 Trajectories
Arosa. Three-dimensional backward trajectories were calculated based on the European Center for Medium-Range Weather Forecasts (ECMWF) wind field using the Lagrangian trajectory tool LAGRANTO (Wernli and Davies, 1997). The 1°×1° spatial resolution of the ECMWF wind field is not adequate to describe the complex flow pattern under upslope conditions in the daytime at an alpine site like Arosa. However, during the nighttime the air flows downward and the air from higher altitudes is less influenced by the complex topography. We therefore use in our analysis only those trajectories which arrive at Arosa at 0600 Universal Time (UTC). For each day five trajectories are calculated for the receptor site, one centered in Arosa and the other four each displaced by 0.5 degree with all arriving at 800 hPa. This pressure is a good approximation for the pressure in Arosa.

Jungfraujoch. ECMWF trajectories for Jungfraujoch are calculated six times per day at 0000, 0400, 0800, 1200, 1600 and 2000 UTC (provided by EMPA). The trajectories are calculated at several heights (850, 830, 810, 790, 770, 730, 710, 690, 670, 650, 630 hPa), among which 650 and 670 hPa are closest to the on-the-spot pressure at the measurement station (about 645-670 hPa).

3.3 Hydrocarbon measurements at Arosa

3.3.1 Overview of the instrument design of AirmoVOC HC1010

Hydrocarbons were measured at Arosa by an automatic gas chromatographic system with a FID detector (AirmoVOC HC1010). During the campaign of PIPAPO, the measurements were compared with several other GC instruments and showed a good precision and accuracy. The detailed description of the instrument can be found in Grüebler (1999). Fig. 3-2 shows a sketch of the instrumental design.

![System of the instrument AirmoVOC HC1010](image)

Fig. 3-2. System of the instrument AirmoVOC HC1010.

The system contains the following parts:

1. Sampling unit: six multisorbent traps packed with 3 cm of Carbopack B for adsorption of C₄-C₁₀ hydrocarbons and 1 cm of Carbosieve III for adsorption of more volatile hydrocarbons. In operation, three traps are located around the drum. One carries out adsorption, another desorption and the third remains idle. The sampling time is 30 minutes, leading to a
3. MEASUREMENTS AND METHODOLOGY

(2) Cryofocusing unit: A fused silica capillary tube packed with 4 cm Carbopack X, which adsorbs hydrocarbons at the ambient temperature and desorbs them at 350 °C.

(3) Separation unit: A fused silica capillary column (12 m × 0.25 mm, BGB 2.5), with a film thickness of 1 µm. The stationary phase consists of mixed apolar material, 2.5% diphenyl- and 97.5% dimethyl-polysiloxan. In operation, the temperature program for the chromatographic separation starts at 35 °C, remains isothermal for 2 minutes, then rises up to 150 °C at a rate of 15 °C per minute and remains isothermal at 150 °C for the last 50 seconds. The carrier gas is hydrogen (5.0).

(4) Detection Unit: a FID detector.

3.3.2 Calibrations

Tedlar bag calibration is applied for the field calibration at Arosa. The calibration is a simple and accurate method for simultaneous calibration of a series of substances (Grüebler, 1999). In practice, liquid standards of 1 µl (Fluka A.G.) are injected by a Hamilton microsyringe into a Tedlar bag (10 l synthetic air, purity of 5.0), yielding an instant evaporation. 150 ml of the standard gas from the Tedlar bag is then injected into the zero air stream flowing to the sampling tubes. The zero air is prepared by sucking in the ambient air through a hydrocarbon filter (for more details see Grüebler, 1999).

It should be noted that the standard gas in Tedlar bags could not be stored for more than 1-2 days as the organic compounds inside can be adsorbed on the tedlar bag wall. The loss of benzene was found to be 10% after 7 days storage.

3.3.2.1 Linearity of the calibration signals

For most of the hydrocarbons there was a good linear correlation between peak areas and sample amounts (see Fig. 3-3). Trimethylbenzenes (TMBs) were not quantified because of the very high memory effects on the sampling trap. The repeated injections of 150 ml samples of 1,2,4-TMB from Tedlar bag led to an increase in the peak areas. They increased from 5000 to 12000 counts in the first four injections and then became constant when it reached about 12000 counts. The poor performance for TMBs was also found in the PIPAPO campaign with errors higher than 20% (Gruebler, 1999). Finally, 14 hydrocarbons were quantified at Arosa, including the hydrocarbons in Table 4-1 and propylbenzene.

In order to monitor the stability of the instrument, the response factors were checked every two weeks during the field measurements by calibration with repeated injections of 150 ml standards. The first sample of xylenes, which normally yields a smaller peak area than those of the following samples, was not considered in the quantification during the calibration.

The detection limit is determined by the six-fold standard deviation of the blank measurements. Since the minimal integrated peak area was set as 100 counts, which was higher than the detection limit, the lower quantification limit was determined based on the sampling volume of 1500 ml. In the field measurements, the lower quantification limits for benzene and m,p-xylene are 5 and 6 ppt respectively. These are based on the response factors on Tube 2 in
August 2002 (52763 and 27920 counts/nmolC), which are typical for all measurements. The values varied from time to time depending on the variation of sampling volume and response factors, see Section 3.3.3.

![Graph showing linear regression lines for different compounds](image)

**Fig. 3-3** Linearity check of selected compounds for the AirmoVOC HC1010 instrument used for hydrocarbon measurements in Arosa. The measurements were carried out in the laboratory prior to the field measurements (10 February 2001).

### 3.3.2.2 Intercomparison of calibration

The dilution of liquid compounds and the handling of the syringe in the preparation of the standard gas in Tedlar bag calibration is potentially error prone. Therefore an intercomparison was performed between the Tedlar bag standard and a commercial 30 component standard gas mixture from the National Physical Laboratory (NPL), England (supplied by EMPA).

Figure 3-4 shows the results of the calibrations on the three tubes. The two systems yielded results in good agreement. However, the performance on Tube 4 was not as good as on the other two tubes. Tube 4 was affected by imperfect sealing, indicated by the deviation of response factors of 3-methylpentane, n-hexane, benzene and n-heptane, which also led to a higher memory effect on Tube 4. The problem is caused by the imperfect position of the drum. However, the position of the drum cannot easily be adjusted after the instrument has been used for more than 10 years. The error was corrected by the blank measurement in the field campaign. The measurements of the blanks were performed before every calibration in the field by means of repeated desorptions of the sampling-free tubes. The measured concentrations were corrected by subtracting the blank values. In Fig. 3-4, the response factors of m,p-xylene were very low, which is related to the condition of the instrument. The reason for this is unclear.
Fig. 3-4. Response factors of several hydrocarbons on Tube 2, Tube 4 and Tube 6, calibrated by the standard gas mixture from the NPL gas and a Tedlar bag on 5 March (see text).
3.3.3 Performance of the instrument in the field measurements

In the long term measurements, the performance of the instrument was not very stable, which is reflected by the response factors (Fig. 3-5) and sampling flow rates (Fig. 3-6). Figure 3-6 also shows the data availability during the measurements.

Three interruptions occurred during the measurements. In the first two interruptions, 30 August - 20 October 2001 (I, indicating the chronological order) and 18 December 2001 – 4 February 2002 (II), the instrument was repaired in Zürich. The first (I) and third interruptions (III, 25 May – 17 June 2002) were caused by lightning strokes.

In December (II), the separation efficiency of the instrument became worse caused by movement of adsorbent inside the precolumn (cryo-trap). Dimethylbutane and n-pentane were not detectable in October to December (see Table 4-1). After changing the precolumn and decreasing the flow rate of the carrier gas, the hydrogen flow rate was adjusted to a smaller value to avoid the movement of the materials in the precolumn.

The lightning stroke on 25 May 2002 (III) destroyed the sensor for flow rate measurements. As it is not easy to replace this part, the instrument was kept running, and the flow rate of the instrument was measured every 2 weeks by hand. The instrument was protected against lightning strokes by a short Teflon tube in the sampling line after May 2002. The smoother line in Fig. 3-6 is from the interpolation of the measured flow rate. The reduction in the flow rate was caused by the abrasion of Teflon fittings, the connection and sealing parts for the sampling tubes.

Response factors (see Fig. 3-5) are related to the sealing of the connection between the sampling tube and precolumn and the sealing of the connection between the precolumn and the separation unit. The position and length of the precolumn also influence the response factors significantly, as shown by the increases in February 2002 after the second repairment.

Fig. 3-5. Response factors of several hydrocarbons on Tube 2 during the measurements.
3. MEASUREMENTS AND METHODOLOGY

3.4 Overview of chemical measurements

The chemical measurements used in this thesis are summarized in Table 3-1. 

**Arosa.** The measurements of inorganic compounds at Arosa are described in the PhD thesis of Campana (2003). The meteorological parameters (temperature, pressure, relative humidity, solar radiation, wind speed and wind direction) were measured at the same site by MeteoSwiss.

**Jungfraujoch.** Trace gas measurements at Jungfraujoch are performed within the Swiss air pollution monitoring network (NABEL). They are part of the Global Atmosphere Watch (GAW) program of World Meteorological Organization (WMO). The applied methods are described in detail by Zellweger et al. (2000). The hydrocarbons (n-pentane, iso-pentane, n-hexane, benzene and toluene) are analyzed by EMPA, with an integration time of 4 hours by GC-MS (Agilent 5793N) which also measures halocarbons (Reimann et al., 2004). The instrument is calibrated with a commercial 30 component standard gas from the National Physical Laboratory (NPL), England.

The two systems for hydrocarbon measurements at Arosa and Jungfraujoch were compared by calibrating the AirmoVOC HC1010 using the NPL standard gas at Arosa, which yielded results in good agreement (see Section 3.3.2). For comparison, hydrocarbon measurements in the center of Zürich also provided by EMPA were also used.
### 3. MEASUREMENTS AND METHODOLOGY

**Table 3-1. Measurements at Jungfraujoch and Arosa**

<table>
<thead>
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<td>Fluorescence</td>
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4 Hydrocarbon concentrations at Arosa and Jungfraujoch

4.1 Introduction

Ozone and its precursors at the remote alpine sites, Arosa and Jungfraujoch, are mainly determined by transport (Pochanart et al., 2001 and Zanis et al., 2002). However, due to the different locations (altitude and topography) of Arosa and Jungfraujoch, the trace gas concentrations have different seasonal and diurnal variations. The meteorological influence on trace gas concentrations have been studied at several measurement stations around the Swiss Alps by Campana (2003). In this chapter, the hydrocarbon concentrations at Arosa and Jungfraujoch are summarized and the different hydrocarbon backgrounds at these two sites are compared. The contributions from the closest sources at the two sites are compared with the hydrocarbon concentrations in Zürich to show the different emission profiles in the closest valleys.

4.2 Seasonal variations of hydrocarbon concentrations

The hydrocarbon concentrations are determined by both the photochemistry and emissions. At the remote sites in the northern hemisphere, the seasonal variations of light alkanes have an identical seasonal variation, which reaches a maximum in late winter and minimum in late summer, which is mainly driven by the variation of OH radicals (Penkett et al., 1993; Klemp et al., 1997; Bottenheim and Shepherd, 1995).

The monthly median concentrations at Arosa and Jungfraujoch are listed in Table 4-1. The seasonal variations of several hydrocarbons which were measured at both Jungfraujoch and Arosa are compared in Fig. 4-1, in which the monthly 25th and 75th percentiles (dashed lines) are shown together with the median concentrations. In February to April, benzene and pentanes had higher concentrations than in other months at both sites. The higher concentrations in winter are most probably caused by the accumulation due to the weaker oxidation rate with lower abundance of the OH radicals. These hydrocarbon monthly median concentrations give results that are consistent with the previous studies.
<table>
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<th>n-heptane</th>
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<th>Toluene</th>
<th>Ethylbenzene</th>
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<td>24.2</td>
<td>-</td>
<td>0.577</td>
<td>1.842</td>
<td>147</td>
</tr>
</tbody>
</table>

\[^1\] n-pentane and dimethylbutane measurements at Arosa in October were not available due to the poor separation. The performance of the instrument was not optimal in the period (see Section 3.3). 

\[^2\] the monthly median is not available because most of the time the concentrations are smaller than the detection limit.
Fig. 4-1. Monthly median concentrations of selected hydrocarbons at Arosa and Jungfraujoch (blue-Arosa, brown-Jungfraujoch). The 25th and 75th percentiles are shown by the dashed lines.
Benzene and pentanes are the slowest reacting compounds measured and therefore they could be accumulated in winter. The accumulation is a global scale phenomenon. However, the faster reacting hydrocarbons did not show any distinct seasonal variations at Arosa. The absence of a seasonal cycle could be due to the fact that reaction rates, even in winter, are high enough to degrade most of the reactive compounds during the transport. In addition, the emissions in the closest valleys are important for the reactive hydrocarbons since the local contribution has much higher concentrations of toluene than the air masses in the background. For example, toluene is determined more by the local emission while benzene is determined by the long range transport. The local emission influence on reactive hydrocarbons was also found at Happo, a coastal site in Japan (Sharma et al., 2000).

Most of time hydrocarbon concentrations at Arosa were higher than those at Jungfraujoch, showing that the contribution of boundary layer emission is higher at Arosa, due to the lower altitude. The higher concentrations of pentanes in December 2001 at Jungfraujoch were due to two special events with downward transport of air masses. The detailed case study is presented in Appendix A. Toluene concentrations at Jungfraujoch are exceptionally high in July and August 2002, which are probably caused by local contamination (see Section 5.4.4).

In addition, monthly medians of NOx and NOy concentrations at Arosa were also much higher than that at Jungfraujoch. The seasonal variation of NOy was not obvious at Arosa while lower concentrations at Jungfraujoch were found in October to February, when the boundary layer emission could be trapped below the temperature inversion. The influence of the temperature inversion is further discussed in Section 5.3. CO concentrations at Jungfraujoch had a seasonal variation, being lower in summer primarily because of enhanced winter time emission by heating. Information relating to the seasonal variation of CO concentrations at Arosa is not available because of extensive periods of data loss in winter and spring. The concentrations of CO at Arosa are, most of time, higher than at Jungfraujoch, but the concentrations in summer 2002 dropped to a lower level, even smaller than the concentrations at Jungfraujoch, which is difficult to explain.

4.3 Diurnal variations of hydrocarbon concentrations

On the slopes of the Alps, the thermal lifting usually takes place every day, except during special weather conditions, like foehn events and the passage of fronts. The airflows in the valley lead to typical diurnal variations (see Fig. 4-2).
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Fig. 4.2 Time series of concentrations of toluene and benzene and the ratios of T/B in August 2001 at Arosa (left) and Jungfraujoch (right).
The maximum concentrations of the reactive hydrocarbons are found at 0800 Central Europe Time (CET) at Arosa, resulting from the thermal lifting of the village emission. The T/B maximum also appears at the same time, showing that these peaks represent air masses from fresh emission at the measurement site. Thereafter, the vertical mixing in the valley becomes stronger, leading to lowest concentrations in the early afternoon. In the late afternoon, an increase in hydrocarbon concentrations is found possibly due to the weakness of the vertical mixing and the decrease of boundary layer height. The late afternoon maximum in hydrocarbon concentrations could also be from the downward transport of air masses from the residual layer above Arosa, which has been found to lead to a peak in ozone at the same time, as described in Staehelin et al. (1994). The air masses in the residual layer have the contributions of other big sources in the closest valleys, like Chur, by up-valley wind transport in the daytime. During the night, the downward transport from higher altitude leads to lower hydrocarbon ratios. The lowest concentrations of hydrocarbons are found in the early morning at about 0600 CET. The diurnal variations of hydrocarbons at Arosa during fair weather days are quite similar to the daily variations previously found under similar weather conditions at Grono in the Mesolcina valley campaign (Prévôt et al., 2000). The high concentrations of hydrocarbons in the late afternoon were less pronounced at Arosa than at Grono. The afternoon high hydrocarbon concentrations at Grono were caused by the air masses from the polluted regions at the mouth of Mesolcina valley, while the emissions from Chur rarely arrive at Arosa by the transport of the valley wind, because of the sharp bending of the valley.

In comparison to the Arosa measurement station, the closest sources of polluted air masses at Jungfraujoch are far from the measurement station. The arrival of the uplifted air masses during fair weather days in summer at Jungfraujoch occurs in the late afternoon, see Fig 4-2. The same diurnal patterns were also found in the aerosol measurements during convective days (Ingold et al., 2001; Lugauer et al., 1998). The injection air from the southwestern valleys 100 km away can also arrive at Jungfraujoch late into the midnight (Lugauer et al., 1998). Although the hydrocarbon peaks are found usually to occur in the late afternoon, the enhancement of hydrocarbon concentrations caused by the up-slope lifting could have already started at midday (Prévôt et al., 1998). The appearance of a maximum in the late afternoon may be caused by weakness of the valley wind at the same time and the following flush by the free tropospheric air.

The very low concentrations of hydrocarbons in the morning at Jungfraujoch also show the clean background, in which the concentrations of trace gases are determined by large scale transport processes. The enhancements of hydrocarbon concentrations by the closest emissions (morning peak at Arosa and late afternoon peak at Jungfraujoch) exhibited large variations, depending on the mixing, synoptic weather condition and the emission intensity.

4.4 Correlations between benzene and other hydrocarbons: The closest sources at Jungfraujoch and Arosa

The contribution of the closest sources can be estimated by the enhancement of hydrocarbons during certain times of the day: The enhancement due to local emission at Arosa ($E_{L,AR}$) is calculated from the mean concentration between 0700 and 0900 CET minus the mean con-
4. HYDROCARBON CONCENTRATIONS

centration between 0500 and 0700 CET, while the enhancement due to the closest emission at Jungfraujoch (EL_JFJ) is calculated from the concentration at 2000 CET minus the concentration at 0800 CET. At Jungfraujoch, the diurnal variations of hydrocarbon concentrations during the convective days are typical for primary pollutants in the summer (Forrer et al., 1998; Schuepbach et al., et al. 2002). Therefore, only the summer cases (June-August 2001 and 2002) are considered, and the enhancements caused by frontal passages are excluded (The detection of fronts is described in Chapter 5). Only the days when EL_AR and EL_JFJ have positive values for all hydrocarbons are considered. In total, 40 days at Jungfraujoch and 72 days in Arosa are investigated for the closest emission contribution.

Table 4-2 shows the correlations between benzene and other hydrocarbons measured in the city center of Zürich in 2001 and the correlations between the closest emission enhancements of benzene and other hydrocarbons at Jungfraujoch and Arosa. The concentration ratios at Zürich are believed to be representative for the ratios of fresh emission in the Swiss Plateau. Several correlation plots are shown in Fig. 4-2. It is remarkable that the correlations between the enhancements at Arosa of benzene and other hydrocarbons, namely n-hexane, n-heptane and toluene, give very similar slopes to those in Zürich. These compounds are mainly from the road traffic emission. In contrast, the slopes between toluene and benzene without the treatment are much lower than those in Zürich, for example, the highest slope of the correlation between toluene and benzene concentrations at Arosa in August 2002 is about 1.7889. The slope for iso-pentane at Arosa is much lower than that for Zürich. The lower iso-pentane concentrations found at Arosa could be caused by the smaller contribution of gasoline evaporation (see Table 1-2) in the rural alpine sites.

| Table 4-2. Slopes, intercepts and squared correlation coefficients (R^2) of correlations between concentrations of benzene (x) and other hydrocarbons (y) at Zürich and those of correlations between enhancements of benzene (x) and other hydrocarbons (y) at Arosa and Jungfraujoch, y=ax+b |
|-----------------|-----------------|-----------------|-----------------|
|                 | Zürich Arosa(N=72) | Jungfraujoch (N=40) |
| iso-butane      | 1.064 6 0.8351 | - - - | 0.935 1 0.7556 |
| n-butane        | 2.222 -63 0.8590 | - - - | 1.645 -1 0.7454 |
| iso-pentane     | 2.213 21 0.7743 | 1.772 7 0.7027 | 2.810 9 0.7701 |
| n-pentane       | 0.778 33 0.8309 | 0.664 9 0.4278 | 1.040 5 0.6775 |
| n-hexane        | 0.258 2 0.8519 | 0.251 2 0.5625 | 0.215 0 0.3990 |
| n-heptane       | 0.258 13 0.6697 | 0.314 1 0.3986 | - - - |
| toluene         | 3.561 64 0.6883 | 3.020 24 0.4280 | 1.352 28 0.1599 |
| ethylbenzene    | 0.487 12 0.8189 | 0.297 6 0.2289 | - - - |
| m,p-xylene      | 1.571 100 0.8103 | 0.683 16 0.1754 | - - - |
| o-xylene        | 0.488 15 0.7981 | 0.348 5 0.3309 | - - - |

However, the slopes of the correlations for the enhancements of butanes and pentanes at Jungfraujoch are close to and even higher than those at Zürich, suggesting that there are other sources, like gasoline evaporation, in the closest valleys.
The hydrocarbon correlations of the closest contribution at both Arosa and Jungfraujoch are generally worse than the correlations of hydrocarbon concentrations in Zürich. The $E_{L,AR}$ values of the most reactive hydrocarbons, ethylbenzene and xylenes, have very poor correlations to $E_{L,JFJ}$ values of benzene, which is related to their high reactivity. The correlation between $E_{L,AR}$ values of toluene and benzene at Jungfraujoch is also very poor. It is worse than the correlations of $E_{L,AR}$ values at Arosa, indicating that the air masses transported from the valleys below are more aged.

![Fig. 4-3. Correlation plots of hydrocarbon enhancements at Arosa (solid circles and black lines) and Jungfraujoch (blank triangles and dash lines). The grey lines are the correlations between hydrocarbons and benzene concentrations in Zürich, which are plotted with 1/10 of the real concentrations, so the intercepts are 1/10 of the b values in Table 4-3.](image)

### 4.5 Conclusions

In this section, the complete dataset of hydrocarbons at Jungfraujoch and Arosa is presented and discussed. The seasonal variations of benzene and pentanes at Jungfraujoch and Arosa are similar. They are higher in winter and lower in summer due to the seasonal variation of photochemistry. The concentrations of reactive compounds like toluene are strongly influenced by the local contribution and do not have clear seasonal variations. The concentrations of hydrocarbons at Jungfraujoch are most of the time much lower than those at Arosa, due
to the smaller contribution of European emissions at Jungfraujoch, which is also shown by the lowest T/B ratios at Jungfraujoch (see Section 5.4).

The hydrocarbon concentrations at Jungfraujoch and Arosa are mainly determined by the long range transport (regional background). The closest emission could be found every day when the thermal circulation is present in the valley. Compared to the regional background, the air masses from the closest sources in the valleys are affected more by the “local” contribution. However, the closest sources are further from the measurement station at Jungfraujoch than at Arosa and the air masses transported by the up-slope wind arrive later and are more aged at Jungfraujoch. In comparison to Zürich emissions, different source contributions of hydrocarbons are found in Arosa and Jungfraujoch. Road traffic emission is found to be the primary source at Arosa, while the closest sources at Jungfraujoch are quite similar to the sources in the urban areas of Zürich.
5 Meteorological influences on trace gas concentrations at Jungfraujoch and Arosa

Several concepts have been developed for the detection of the free tropospheric air in studies on trace gas behaviors, in-situ photochemistry and the background ozone trend (Zellweger et al., 2000; Zanis et al., 1999; Schüepbach et al., 2000). These criteria include the concentrations of selected primary pollutants and some meteorological parameters, such as relative humidity, wind speed and direction. Zellweger et al. (2002) provided a meteorological classification for the study of the variability of NO\textsubscript{y} concentrations and its partitioning at Jungfraujoch. The meteorological conditions were classified into four categories: undisturbed free troposphere, foehn events, synoptic lifting and thermally induced vertical transport. The classification is also thought to be applicable for other alpine sites. However, at Arosa, the influence of the boundary layer on the trace gas concentrations is more complex and difficult to be described simply by the weather classification. This is due to the venting caused by topography over the alpine region and the contribution of mixing during long range transport.

In this chapter, fronts and anticyclonic conditions with temperature inversions are investigated carefully and the trace gas transport and transformation will be discussed in detail. Firstly, the frontal influences on trace gas concentrations at Jungfraujoch are investigated in Section 5.1 and the simultaneous trace gas concentrations at Arosa are compared to the concentrations at Jungfraujoch in section 5.2. Secondly, the transport processes of air masses at Arosa in winter are studied in section 5.3, highlighting the influence of temperature inversions on trace gas concentrations at Arosa and Jungfraujoch. The transports above the temperature inversion are studied by a trajectory approach, which was applied to ozone in Arosa in Pochanart et al. (2001). Finally, in Section 5.4, the free tropospheric air masses at Jungfraujoch are detected by the ratios between two hydrocarbons, and the free tropospheric OH concentration in the intercontinental transports is estimated from the degradation of the hydrocarbons.

5.1 Influenced of the meteorology on trace gas concentrations at Jungfraujoch

5.1.1 Detection of fronts

Forrer et al. (2000) have used certain parameters in Alpine Weather Statistics (AWS) to detect the frontal passage over Jungfraujoch. The AWS was developed by Schüep (1979) to study typical weather sequences and the climate change in a region, centered at Rheinwald-
horn (46 N, 9 E) with a radius of 222 km, which covers the Swiss plateau in an east-west range from Geneva to Zugspitze (Wanner, 1998). The AWS weather classes include 40 weather situations, which are grouped into 8 weather types, based on the surface and 500 hPa pressure field (Table 6-2). Among the parameters in AWS, the parameters 18 and 21 indicate frontal passage in Zürich which is detected by weather charts, temperature change and the mean precipitation (Forrer et al., 2000). However, this method is not very accurate, since the fronts may decay on their way from Zürich to the alpine region (Campana, 2003). In this section, the fronts are detected based on the local meteorological information, primarily relative humidity (> 80%) and the Berlin weather charts. The temperature decrease is used as a criterion for the detection of cold fronts. The weather condition analysis for all days in the period of September 2001-August 2002 is shown in Table App-1. The warm and occluded fronts are called weak fronts in this classification.

5.1.2 Trace gas concentrations under the frontal influence

Figure 5-1 provides a case study of the meteorological influence on the trace gas concentrations at Jungfraujoch. The period of 16-31 April 2002 was selected because it contained three individual fronts (indicated by the shaded periods) and there were large variations of trace gas concentrations. The influence of the frontal passage on the trace gas concentrations for the three fronts is discussed.

The first occluded front reached Jungfraujoch in the midnight of 16-17 April together with low temperature and enhanced relative humidity. Before the arrival of this front, a low pressure system had stayed over the alpine region for three days (14-16 April) and the previous cold front had arrived at Jungfraujoch from the south direction on 14 April. The front at midnight of 16-17 April carried up much polluted air with high concentrations of CO, NO\textsubscript{y} and benzene. However, the ratios of T/B were lower than those in the following cleaner days (see the decreasing of CO concentrations), indicating that the air masses from the boundary layer had already aged during the frontal passage. The aging could have happened whilst the air masses remained in the Alpine region. Thereafter, the concentrations of CO, toluene and benzene strongly dropped on 18 April. The concentrations of primary pollutants increased sharply, caused by the lifting just ahead of the second front, when the wind direction changed to S-SE in the late afternoon of 18 April.

The second cold front came from the N-NW direction in the late afternoon of 19 April. This front came between two events originating from the south, which carried much higher concentrations of primary pollutants, so the influence was not as pronounced as the first one. At midnight of 21-22 April and at 1200 CET 23 April, there were two cases of very low relative humidity with simultaneous decreases in the concentrations of benzene and CO, as well as very low ln(toluene/benzene). These cases were caused by the downward transport of the very clean free tropospheric air, according to the ECMWF trajectories. However, the first air masses were diluted into the polluted air masses from the south. That had been lifted upward on 21 April. This explains the higher concentrations of primary pollutants.
Fig. 5-1. Weather conditions and the trace gas behaviors at Jungfraujoch in 16-30 April 2002. The shaded areas show the possible time of frontal passage, based on the weather information (see Section 5.1.1).

The third warm front passed on 24 April with no temperature change but enhanced relative humidity. The air was from fresher emission in comparison with the first two cases, indicated by the higher toluene/benzene ratios. At midday on 27 April, there was another event of downward transport of free tropospheric air. Thereafter, the concentrations of primary pollutants, primarily toluene and NOy, had a regular diurnal variation with the maximum in the late afternoon, which is the typical variation induced by the thermal circulation at Jungfraujoch (Zellweger et al., 2000). The relative humidity and ozone concentration also showed a maximum in the late afternoon. The ratios of toluene/benzene were sometimes constant at a high level and no decrease was found over night at Jungfraujoch (the weak frontal disturbance in April described in Section 5.2 and the summer case described in Section 6.5.2), which shows
that the nighttime residual layer is not replaced by the free tropospheric air. Similar conditions were also found during indifferent convective days by Zellweger et al. (2000), through the ratios of NO$_y$/CO.

At Jungfraujoch, days of high relative humidity are always found around frontal disturbances. On these days, trace gases show similar behaviors to either those in frontal days or those in convective days.

The concentrations of primary pollutants as a function of relative humidities (RHs) in the period of 16-30 April are given in Fig. 5-2. The air masses of high relative humidity are more polluted, which also suggests that relative humidity is a suitable criterion to describe the disturbance of the boundary layer (Schuepbach et al., 2001), though the correlations between trace gas concentrations and RHs are very weak. The values of ln(T/B) and NO$_y$ concentrations have the best correlation to RHs. There is no direct correlation however, between ln(T/B) and NO$_y$, with the highest values of ln(T/B) and NO$_y$ determined by the local the synoptic influence individually.

The variation of trace gas concentrations indicates various boundary layer influences, caused by the following factors: i) the boundary layer disturbance produces different patterns, as shown above; ii) NO$_y$ concentrations are influenced by the wet deposition, and most importantly, iii) the synoptic lifting (e.g. a cold frontal passage) carries up the aged air, but with large amounts of primary pollutants while the weak fronts transport the boundary layer air masses on a smaller scale from the fresh emission in the valley (Although the first front was not a cold front, the trace gas concentrations have characteristics of the synoptic transport.).

![Fig. 5-2. Correlations between trace gas concentrations as well as ln(toluene/benzene) and relative humidities at Jungfraujoch during 16-30 April.](image-url)
The comparison gives further evidence that the background levels at Arosa and Jungfraujoch are very different. Only during the large scale transport events like the passage of cold fronts, the two sites are possibly under similar conditions. The difference is caused by the alpine air flow, as discussed in Section 4.
5.3 Transport processes of ozone and its precursors to the measurement stations, Arosa and Jungfraujoch in winter 2001-2002

Tropospheric ozone at Arosa is strongly dependent on the transport process. Pochanart et al. (2001) found that European emissions contribute to ozone concentrations at Arosa, posi-
5. Meteorological Influences

This section investigates the influence of weather conditions on the contributions of the European boundary layer and hemispheric background in the winter season. First of all, the trapping effect of the temperature inversion over the Swiss Plateau in winter is documented. Then, the contribution of European emissions to ozone at Arosa during the period of persistent temperature inversion is investigated. Finally, the influence of the temperature inversion is also studied at Jungfraujoch, focusing on the free tropospheric air masses from different origins.

5.3.1 Trace gas concentrations at Arosa and the influence of the temperature inversion

Weather conditions have a strong influence on the distribution of primary pollutants in the alpine region. Figure 5.4 shows the mean diurnal variation of ozone and its precursors (30 min integration) in winter 2001-2002. The measurements are classified according to average daytime relative humidity (RH, average of 0600 to 1800 CET), < 60% and > 80% (“fair weather type” and “frontal type”, respectively). As shown in the Fig. 5.5, the air masses at Arosa and Jungfraujoch were much cleaner with respect to primary pollutant concentrations during good weather days (16-22 November) when a persistent temperature inversion occurred over the Swiss Plateau.

The lowest concentrations of the primary pollutants were found between 0400 and 0800 CET in the morning and the primary pollutant concentrations on the dry days showed typical diurnal variations, increasing at around 0900 and decreasing at around 1800 CET (see Fig. 5.4). This was caused by the thermal valley wind. However, the concentrations of the primary pollutants have no obvious diurnal variations due to the very weak solar radiation. The local emission, which appeared in the daytime, had no obvious influence on ozone concentrations. In contrast to the summer diurnal variations (Fig. 4.2), the mixing in winter at midday is much weaker and there was no drop of primary pollutant concentrations in the early afternoon.

The concentrations of ozone during days classified as the fair weather type were considerably higher than during the days of the frontal type. The primary pollutants, benzene and CO which have a longer lifetime showed opposite tendencies. The increased primary pollutant concentrations are attributed to the mixing with air masses from the polluted planetary boundary layer. The nighttime concentrations of NO$_y$ and toluene, which are determined by the regional background, also appeared to be lower in fair weather days and higher in frontal days, like CO and benzene. However, concentrations of NO$_x$, NO$_y$ and toluene were not very different for the two weather classes during the daytime. The daytime concentrations have the contribution from the local thermal lifting, which is stronger during fair weather days. The similar concentrations of the short lived compounds during the daytime are determined by the stronger thermal lifting under fair weather conditions.
Fig. 5-4. Mean diurnal variations of trace gas concentrations averaged in the period of November 2001 to January 2002 at Arosa. The solid points are from the days of mean daytime RH > 80%, the blank points from days of mean daytime RH < 60% and the thick line shows the average of all days.
Fig. 5-5-1. Concentrations of ozone and its precursors at Arosa in the second part of November 2001. The black arrows show the periods of frontal passages.
5. METEOROLOGICAL INFLUENCES

Fig. 5-5-2. Concentrations of ozone and its precursors at Jungfraujoch in the second part of November 2001. The grey arrows show the time of polluted southerly wind and the black arrows show the time of the frontal passage. The three periods of the free troposphere air from different origins (discussed in Section 5.3.3) are indicated by a (0000 CET, 3 November to 0000 CET, 6 November), b (0000 CET, 17 November to 0000 CET, 20 November) and c (0400 CET, 20 November to 0400 CET, 22 November).

The strong influence of the persistent inversion layer is further demonstrated by the comparison of NO\textsubscript{x} and O\textsubscript{3} concentrations at seven sites in Switzerland. In Campana’s thesis (2003), six sites in the NABEL monitoring network, Duebendorf (430m), Taenikon (540m), Rigi (1030m), Chaumont (1140m), Davos (1590m) and Jungfraujoch (3580m) were investigated together with Arosa in November. The mean O\textsubscript{3} and NO\textsubscript{x} concentrations during the temperature inversion period (16-22 November) are compared with the monthly means of the seven sites. Figure 5-6 shows the trapping effect of the temperature inversion. The inversion layer was located at an altitude between Chaumont and Davos, thus between 1140 and 1590 m. As expected, NO\textsubscript{x} concentrations below the inversion layer were higher than the monthly...
mean and O₃ concentrations were lower than the monthly mean. The concentrations of ozone and NOₓ above the temperature inversion showed an opposite tendency.

NOₓ concentrations still showed a significant gradient above the inversion layer. This could be explained by the thermal up-slope air, which can penetrate the inversion layer, leading to the vertical transport of the primary pollutants. The thermal circulation can also be found by the increase in the concentrations of hydrocarbons during the daytime for 16-21 November (see Fig. 5-5-1). Such a contribution of boundary layer to the air above the inversion layer was previously found at Chaumont, February 1993 (Brönnimann and Neu, 1998), by the diurnal NO₂ and ozone cycles.

![Graph](image.png)

**Fig. 5-6.** The monthly mean NOₓ and ozone concentrations (squares) in November 2001 and the mean concentrations during the period of a persistent temperature inversion over the Swiss Plateau (diamonds) from 16 to 22 November. The thick grey line shows the temperature inversion above the Swiss Plateau. The right top figure shows NOₓ concentrations on a logarithmic scale, after the PhD thesis of Campana (2003).

## 5.3.2 Trajectory analysis

### 5.3.2.1 Separation of air masses

Based on the understanding of the weather influences at Arosa (see Section 3), the trajectory approach, which has been used by Pocharnart et al. (2001), is applied to analyze the regional backgrounds under fair and frontal conditions (Section 4.2). The fair weather days were separated by the daytime average RH < 80% (0600-1800 CET). A time window (0500-0700 CET) is also used since background air is normally found during the night, as discussed in Section 5.3.1 and the trajectories are more accurate in the downward transport in the morning. Some chemical filters are also applied to detect and separate the local emission contribution, which was occasionally present in Arosa from the nearby human activities in the skiing areas.

The chemical composition measured at the sampling sites includes further information related to the history of the air masses. The ratio of NOₓ/NOᵧ contains information about the
oxidation state. Trainer et al. (1993) suggested that \( \text{NO}_x/\text{NO}_y < 0.5 \) is representative for photochemically aged air. In this work \( \text{NO}_x/\text{NO}_y < 0.5 \) and \( \text{CO} < 150 \text{ ppb} \) are used to determine aged air masses without local influence at Arosa. Furthermore, the toluene/benzene ratio less than the 25th percentile of the month, is used complementarily at Arosa in case no CO measurements were available due to technical problems with the CO analyzer.

The chemical filters also help to discriminate between the two kinds of weather conditions. After separation, two periods in November, 3-5 and 16-22 are found to belong to the fair weather type.

5.3.2.2 European contribution to ozone at Arosa in winter

For summer conditions, a positive correlation between ozone concentrations at Arosa and residence times over Europe was found by Pochanart et al. (2001). The extrapolation of the assumed linear relation to the zero residence time was believed to represent the background ozone over the Atlantic Ocean. In this section, the method is further applied to the measurements at Arosa in winter.

The residence time of trajectories is calculated and the area of Europe is determined by the land-sea mask in the range of –10° to 20° longitude and 35° to 60° latitude. Most of the trajectories during fair weather days are found at the heights above 850 hPa. Figure 5-7 shows the correlation between concentrations of ozone and benzene and residence times in winter and spring. Benzene is a more suitable indicator to show the European contribution in winter than any other compound because of its long lifetime of about 10 days. It has to be noted that we did not follow the general separation of seasons (winter – from December to February) because the persistent temperature inversions were found only in November to January (winter). The correlation between ozone concentrations and European residence times is positive with a slope of about +1.34 ppb/d in winter and +2.76 ppb/d in spring during fair weather days. The enhanced rate of ozone increasing along the trajectories in spring indicates increased photochemical production of ozone. Benzene concentrations under fair weather conditions in winter were very low and they had no relation to the residence times. However, they show an obvious tendency to increase, along with longer residence times in spring, which indicates the higher contribution of European emission.

The polluted planetary boundary layer over Europe is known to be a net \( \text{O}_3 \) sink during winter (Derwent et al., 1998). The decrease of ozone concentrations during frontal days in winter (dashed line in Fig. 5-7) is related to the advection of polluted planetary boundary layer air. However, in the free troposphere, the net ozone production rate is positive (Yienger et al., 1997). The photochemical ozone production at 40-50° N, 685 hPa in spring was estimated to be about +0.3 ppb/d by a three-dimensional global chemical transport model (GCTM). The ozone production in the free troposphere has been widely studied at the remote locations, and the net ozone production, dependent on \( \text{NO}_x \) concentrations, varied greatly at different regions (Zanis et al., 2000; Jaeglé et al., 1998). The midday net ozone production in the free troposphere at Jungfraujoch in March was found to be +0.09 ppb/h by Zanis et al. (2000). It is about +0.7 ppb/d, when accounting for the time for photochemical oxidation, which is considered to be about 8 hours. The enhanced ozone production rate (1.34 ppb/d) in winter at Arosa is possibly due to the vertical dilution of ozone precursors over alpine areas,
where the up-slope wind can penetrate the inversion layer. The input of small amounts of ozone precursors increases the ozone production during the transport. Carpenter et al. (2000) estimated that NO concentration is about 10 ppt at the balance of ozone formation and destruction in January at Jungfraujoch. The mean NO concentrations at Arosa during fair weather days are 386 ppt, which could lead to ozone formation. The photochemical ozone formation rate at Chaumont in February 1993 by Brönnimann et al. (1998) was found to be about 1.4 ppb/d, quite similar to the result obtained by trajectory analysis at Arosa.

Fig. 5-7. Correlations between ozone concentrations and residence times over Europe (November-January (upper) and February-April (lower), see text). Solid black diamonds – fair weather days; solid grey diamonds – frontal days; blank diamonds – other days. The black and the dashed line are the correlation lines for ozone concentrations of the fair weather type and frontal type respectively.

5.3.3 Case Studies in November 2001 at Jungfraujoch: influence of long range transport

In Fig. 5-5-2, the air at Jungfraujoch during the days with a persistent temperature inversion above the Swiss plateau is the “undisturbed free troposphere” as defined by Zellweger et al. (2002). Three periods in these days are separated out based on a synopsis of the available information. The 670 hPa ECMWF trajectories of the air masses in the three periods are shown in Fig. 5-8. The air masses in the three periods originated from the North Atlantic ma-
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rine boundary layer (a), continental boundary layer of North Africa (b) and North America (c), respectively. The mean trace gas concentrations during the three periods are summarized in Table 5-1. Among the three cases, the air from North Africa had highest ozone concentrations. The air masses are possibly from the polluted surface area Tripolis, in North Africa, together with large amounts of ozone precursors. The air from America had highest concentrations of primary pollutants (benzene and CO), although it was also the most aged, as indicated by the toluene/benzene ratios. The air from the marine boundary layer over North Atlantic was much cleaner compared to the other two cases.

The trajectory approach helps to obtain information on the contribution of European anthropogenic emissions. The residence time is calculated as the mean residence time from 18 trajectories using two arrival heights (650, 670 hPa) at Jungfraujoch. The correlations between ozone and benzene concentrations and the residence times are shown in Fig. 5-9.

The trajectories in case (a) (See Fig. 5-8) showed that the air parcels stayed over the alpine region before arriving at Jungfraujoch. The concentrations of ozone and benzene increased strongly during the transport in this event (see Fig. 5-9). The increase in benzene concentrations suggests that European ozone precursors, mixed into the air arriving at Jungfraujoch, had an influence and hence improved the ozone formation. The temperature inversion during these days was not very strong referring to the vertical profile of equivalent potential temperature from the Payerne sounding. The weak temperature inversion to some extent explains the vertical transport of European emission in case (a). In the third case (c) (see Fig. 5-9), only the ozone concentrations are enhanced with a small slope, 0.79 ppb/d, which is close to the spring ozone formation rate at Jungfraujoch found by Zanis et al. (2000). The constant concentrations of benzene suggest that there is no contribution of European emission. The very low toluene/benzene ratio in this case (see Table 5-1) is characteristic of intercontinental transport from North America to Jungfraujoch, because the air masses had stayed in the upper troposphere for over 5 days. This is only one of the intercontinental transport events in winter 2001. All the intercontinental transport events will be investigated in the next section using the information from hydrocarbon ratios. Case (b) also shows similar tendency of ozone and benzene upon residence times as case (c), although the correlations are much worse. In case (b) and case (c) the residence times should be determined by the transport times from the source region to Jungfraujoch, but the values of these times are difficult to obtain, because of the complex transport process. To some extent, the European residence times can be used instead of the transport times from the source regions to Jungfraujoch.
Fig. 5-8. Origins of the “undisturbed free tropospheric” air masses in November at Jungfraujoch (0000 and 1200) (see text). (a) 0000 3 November - 0000 5 November; (b) 1200 17 November – 1200 19 November; (c) 1200 20 November – 0000 22 November. Red marks show time intervals of 24 hours. The color bar shows the altitude of the trajectories.
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Table 5-1. Mean concentrations of ozone and its precursors in the three cases of free tropospheric air from different origins arriving at Jungfraujoch in November 2001.

<table>
<thead>
<tr>
<th>Origins</th>
<th>CO (ppb)</th>
<th>ozone (ppb)</th>
<th>NO\textsubscript{y} (ppb)</th>
<th>NO\textsubscript{x} (ppb)</th>
<th>benzene (ppt)</th>
<th>toluene (ppt)</th>
</tr>
</thead>
<tbody>
<tr>
<td>a Atlantic marine boundary layer</td>
<td>81.32</td>
<td>42.93</td>
<td>n.a.</td>
<td>n.a.</td>
<td>24.00</td>
<td>22.51</td>
</tr>
<tr>
<td>b North Africa</td>
<td>108.82</td>
<td>50.85</td>
<td>0.42</td>
<td>0.17</td>
<td>47.25</td>
<td>32.33</td>
</tr>
<tr>
<td>c North America</td>
<td>114.47</td>
<td>49.24</td>
<td>0.31</td>
<td>0.07</td>
<td>54.28</td>
<td>12.94</td>
</tr>
</tbody>
</table>

n.a.: no measurements available.

\[
y = 1.603x + 39.922 \\
R^2 = 0.2631
\]

\[
y = 0.7936x + 47.826 \\
R^2 = 0.5978
\]

\[
y = 0.7936x + 47.826 \\
R^2 = 0.5978
\]

\[
y = 1.603x + 39.922 \\
R^2 = 0.2631
\]

Fig. 5-9. Correlations of concentrations of ozone and benzene to the residence times over Europe at Jungfraujoch in the three cases of “undisturbed free tropospheric” air in Fig 5-8. Black diamonds - case (a), grey triangles - case (b), blank squares - case (c). The statistically significant correlations (\textit{t}-test p-value is smaller than 0.1) are shown by the solid lines and the equations are given beside the lines.

Although the air in these three cases is “undisturbed free tropospheric air”, the European emission possibly still contributed to ozone at Jungfraujoch in case (a), which shows that even the high measurement station Jungfraujoch is not completely decoupled from the alpine
boundary layer during the fair weather days in winter. In contrast, the air masses in case (b) and case (c) are most possibly the free tropospheric air without European contribution.

5.4 Hydrocarbons in the free troposphere

5.4.1 Ratios of pairs of hydrocarbon concentrations at Jungfraujoch and Arosa

The concentration ratios of hydrocarbons of different reactivities contain valuable information on the oxidation state of the air masses and hence the “age” of air masses (see Section 2.2). The more reactive hydrocarbons are degraded faster during the long range transport. The frequency distributions of toluene to benzene ratios (Fig. 5-10) clearly indicate that the oxidation state of air masses at Zürich is the lowest, whereas the most oxidized air masses are found at Jungfraujoch. The distribution of the ratios at Arosa is more compact compared to that at Jungfraujoch. The lowest toluene/benzene concentrations at Jungfraujoch suggest that the air masses at Jungfraujoch have a smaller contribution of European emissions than at Arosa.

The most aged air masses (determined by toluene/benzene ratios) mostly occurred in the winter season concurrent with decreasing relative humidities because of the weak vertical mixing above the temperature inversion (Zellweger et al., 2000). The backward trajectories show that the most aged air masses have an average altitude of about 450 hPa during the previous 10 days. In the period of October to January, about 11% of the air masses (86 cases) have their ratios of toluene/benzene smaller than 0.5, among which only 7 cases could have the contribution of stratospheric intrusion. This was determined by applying the criterion of PV > 2 (representative for the tropopause, see e.g. Brunner et al., 1997). In the following sections, the air masses with lowest toluene/benzene ratios are analyzed with trajectories and the OH concentration in them is estimated.

![Graph](image)

**Fig. 5-10.** Frequency distributions of toluene/benzene in Zürich, Arosa and Jungfraujoch. Data are from July 2001 to August 2002

5.4.2 Cases of transatlantic transport and hydrocarbon concentrations in them
5. METEOROLOGICAL INFLUENCES

Backward trajectories from a compact area often disperse after a few days in the backward direction (e.g., Stohl et al., 2002). In the section, the surface origins of air masses are detected by ECMWF trajectories arriving at 670 hPa for Jungfraujoch (5 trajectories, one at 46.55°N, 9.65°E and four displaced by 0.5° in each cardinal direction). A criterion is used in the identification of the source region of the free tropospheric air. The three dimensional dispersion of the five trajectories (\(\sigma\)) is defined as

\[
\sigma = \ln \left[ \frac{\sum_{i=1}^{5} |x_i(t) - \bar{x}(t)|}{\sum_{i=1}^{5} |x_i(0) - \bar{x}(0)|} \right],
\]

where \(\bar{x}(t)\) is the location of the average trajectory at time \(t\) and \(x_i(t)\) is the location of the \(i\)-th trajectory at time \(t\) (Liniger, 2002). The air masses with \(\sigma\) less than 3.5 before reaching 800 hPa are considered to come from a compact source region. In particular, if there is only one trajectory leaving the ensemble of five trajectories before the center one reaches the altitude of 800 hPa, the air mass is still thought to be emitted from compact surface sources. Only in these cases can the hydrocarbon degradation be estimated by the residence time in the free troposphere. The air masses in Fig. 5-11(a) are an example of free tropospheric air masses having compact surface sources.

5.4.3 Estimate of OH concentration in the transatlantic transport

Table 5-2 gives the concentrations of hydrocarbons and CO during the detected intercontinental transport. The degradation of hydrocarbons in the free troposphere over the ocean occurs primarily through oxidation by OH and Cl (Wingenter et al., 1998). The corresponding reaction rates are listed in Table 5-3. The correlation between hydrocarbon concentrations and residence times are also included in Table 5-3. The toluene concentrations of 17 and 18 October are however not included since the toluene concentrations can be influenced by the local contamination at Jungfraujoch, as will be discussed in Section 5.4.4. The slopes of the correlation lines are degradation rates of these hydrocarbons (refer to equations in Section 2.2). The closer degradation rates of i-butane and benzene suggest that OH oxidation is the primary degradation mechanism for the hydrocarbons, since the oxidation rate of benzene by Cl is very low. Although the degradation rate of n-butane is similar to those of pentanes, the similarity is possibly caused by quite similar reaction rates of OH oxidation.

According to the theory of McKeen et al. (1993), the decrease of hydrocarbon concentrations during the transport in the remote free troposphere is comprised of two processes: dilution and oxidation (see equation 2-10). For hydrocarbons of zero background, the correlation slopes in Table 5-3 correspond to \([\text{OH}]k_{\text{OH}} + K\). The slope and the intercept of the plot of Fig. 5-12, \([\text{OH}]k_{\text{OH}} + K\) as a function of \(k_{\text{OH}}\), are the dilution rate and the OH concentration respectively. From this plot, one can conclude that the OH concentration in the free troposphere is about \(5.1 \times 10^5\) cm\(^{-3}\) and the dilution rate is 0.0034 hr\(^{-1}\) in these intercontinental transport events. The OH concentration can also be estimated from the correlation between the logarithms of the concentration ratios of two hydrocarbons and the residence times (not shown here), which gives the OH concentration in the range of 4.5 – 6.7 \(\times 10^5\) cm\(^{-3}\).
The OH concentration during the intercontinental transport cases is quite similar to that found over the Atlantic Ocean in PEM WEST B., March 1996 (Ehhalt et al., 1998), in which OH concentration was $6 \times 10^5$ cm$^{-3}$ in the free troposphere. Because the warm conveyor belt could carry large amounts of radical precursors, like water, and oxygenated organic compounds (Wennberger et al., 1998), the estimated OH concentration could be viewed as the upper limit of the OH concentrations in the winter free troposphere.

**Fig. 5-11.** 15 days backward ECMWF trajectories for two cases of the free tropospheric air arriving at Jungfraujoch. Trajectories in (a) show the surface source of the air masses reaching Jungfraujoch, while trajectories in (b) show that there was no clear surface origin of the air masses. The color scale shows the altitude of the trajectories.
### Table 5-2. The cases of very low toluene/benzene ratios at Jungfraujoch with the concentrations of hydrocarbons and CO in the individual cases and the residence time from the surface sources to Jungfraujoch, in the period of October 2001 to January 2002.

<table>
<thead>
<tr>
<th>Time (UTC)</th>
<th>CO (ppb)</th>
<th>i-butane (ppt)</th>
<th>n-butane (ppt)</th>
<th>iso-pentane (ppt)</th>
<th>n-pentane (ppt)</th>
<th>n-hexane (ppt)</th>
<th>benzene (ppt)</th>
<th>toluene (ppt)</th>
<th>residence time (hr)</th>
</tr>
</thead>
<tbody>
<tr>
<td>10/17/2001 2000</td>
<td>85.54</td>
<td>44.22</td>
<td>53.49</td>
<td>30.08</td>
<td>14.66</td>
<td>3.79</td>
<td>31.73</td>
<td>15.50</td>
<td>235</td>
</tr>
<tr>
<td>10/18/2001 0000</td>
<td>86.35</td>
<td>42.01</td>
<td>50.38</td>
<td>26.28</td>
<td>13.28</td>
<td>3.45</td>
<td>30.42</td>
<td>9.20</td>
<td>268</td>
</tr>
<tr>
<td>11/20/2001 0400</td>
<td>112.05</td>
<td>110.44</td>
<td>241.65</td>
<td>92.37</td>
<td>56.11</td>
<td>21.79</td>
<td>62.66</td>
<td>11.24</td>
<td>91</td>
</tr>
<tr>
<td>11/20/2001 0800</td>
<td>122.29</td>
<td>97.02</td>
<td>234.79</td>
<td>79.30</td>
<td>47.07</td>
<td>18.09</td>
<td>59.64</td>
<td>18.04</td>
<td>107</td>
</tr>
<tr>
<td>11/21/2001 0000</td>
<td>115.66</td>
<td>86.47</td>
<td>155.23</td>
<td>55.01</td>
<td>36.90</td>
<td>12.62</td>
<td>53.95</td>
<td>8.81</td>
<td>124</td>
</tr>
<tr>
<td>11/21/2001 0400</td>
<td>114.76</td>
<td>99.30</td>
<td>287.55</td>
<td>77.47</td>
<td>45.90</td>
<td>16.22</td>
<td>55.22</td>
<td>7.90</td>
<td>119</td>
</tr>
<tr>
<td>11/21/2001 1200</td>
<td>109.04</td>
<td>86.72</td>
<td>157.59</td>
<td>52.63</td>
<td>36.59</td>
<td>12.63</td>
<td>52.99</td>
<td>7.82</td>
<td>133</td>
</tr>
<tr>
<td>11/22/2001 0000</td>
<td>115.66</td>
<td>86.47</td>
<td>155.23</td>
<td>55.01</td>
<td>36.90</td>
<td>12.62</td>
<td>53.95</td>
<td>8.81</td>
<td>124</td>
</tr>
<tr>
<td>11/22/2001 0800</td>
<td>114.76</td>
<td>99.30</td>
<td>287.55</td>
<td>77.47</td>
<td>45.90</td>
<td>16.22</td>
<td>55.22</td>
<td>7.90</td>
<td>119</td>
</tr>
<tr>
<td>12/9/2001 0000</td>
<td>149.70</td>
<td>106.91</td>
<td>231.96</td>
<td>223.59</td>
<td>80.73</td>
<td>32.97</td>
<td>70.86</td>
<td>13.30</td>
<td>87</td>
</tr>
<tr>
<td>12/9/2001 0400</td>
<td>n.a.</td>
<td>85.77</td>
<td>172.58</td>
<td>155.94</td>
<td>59.69</td>
<td>26.44</td>
<td>71.41</td>
<td>25.25</td>
<td>74</td>
</tr>
<tr>
<td>12/24/2001 0800</td>
<td>119.68</td>
<td>118.57</td>
<td>211.64</td>
<td>79.90</td>
<td>60.25</td>
<td>20.86</td>
<td>76.47</td>
<td>11.23</td>
<td>163</td>
</tr>
<tr>
<td>1/3/2002 2000</td>
<td>126.21</td>
<td>152.43</td>
<td>315.85</td>
<td>121.37</td>
<td>88.68</td>
<td>36.41</td>
<td>103.87</td>
<td>23.85</td>
<td>67</td>
</tr>
<tr>
<td>1/4/2002 0000</td>
<td>123.25</td>
<td>146.80</td>
<td>314.11</td>
<td>138.56</td>
<td>75.72</td>
<td>35.69</td>
<td>91.74</td>
<td>25.01</td>
<td>72</td>
</tr>
<tr>
<td>1/4/2002 0400</td>
<td>125.08</td>
<td>155.94</td>
<td>331.08</td>
<td>145.06</td>
<td>85.32</td>
<td>37.90</td>
<td>101.24</td>
<td>23.89</td>
<td>79</td>
</tr>
<tr>
<td>1/4/2002 0800</td>
<td>128.63</td>
<td>162.48</td>
<td>368.09</td>
<td>134.51</td>
<td>88.86</td>
<td>33.06</td>
<td>97.86</td>
<td>31.72</td>
<td>85</td>
</tr>
<tr>
<td>1/4/2002 1200</td>
<td>137.19</td>
<td>136.92</td>
<td>305.96</td>
<td>113.06</td>
<td>78.29</td>
<td>29.31</td>
<td>95.31</td>
<td>37.95</td>
<td>88</td>
</tr>
</tbody>
</table>

### Table 5-3. Reaction rates of hydrocarbons by Cl (kCl) and OH (kOH) at 0°C, and the correlation between concentrations and residence times

<table>
<thead>
<tr>
<th>Hydrocarbons (X)</th>
<th>kOH ( (\times 10^{-12} \text{cm}^{-3} \text{s}^{-1}) )</th>
<th>kNO ( (\times 10^{-15} \text{cm}^{-3} \text{s}^{-1}) )</th>
<th>kCl ( (\times 10^{-10} \text{cm}^{-3} \text{s}^{-1}) )</th>
<th>Correlations between ln(X) and residence times</th>
</tr>
</thead>
<tbody>
<tr>
<td>i-butane</td>
<td>1.97</td>
<td>-</td>
<td>1.40</td>
<td>-1.67</td>
</tr>
<tr>
<td>n-butane</td>
<td>2.14</td>
<td>6.5</td>
<td>1.91</td>
<td>-2.55</td>
</tr>
<tr>
<td>iso-pentane</td>
<td>3.35 (^5)</td>
<td>-</td>
<td>1.94</td>
<td>-2.50</td>
</tr>
<tr>
<td>n-pentane</td>
<td>3.55</td>
<td>8.0</td>
<td>2.46</td>
<td>-2.58</td>
</tr>
<tr>
<td>n-hexane</td>
<td>5.09</td>
<td>10.5</td>
<td>3.44</td>
<td>-3.33</td>
</tr>
<tr>
<td>benzene</td>
<td>1.16</td>
<td>3.2</td>
<td>0.04 (^4)</td>
<td>-1.54</td>
</tr>
<tr>
<td>toluene</td>
<td>5.64</td>
<td>6.9</td>
<td>0.56 (^3)</td>
<td>-4.11</td>
</tr>
</tbody>
</table>

\(^1\) Atkinson et al., 2000.  
\(^2\) reaction rates at the ambient temperature, Wayne et al., 1991.  
\(^3\) Qian et al., 2001.  
\(^4\) Wallington et al., 1988.  
\(^5\) estimated by the change of n-pentane’s reaction rate from 298 K to 273 K, because no information on the temperature-dependence reaction constant for iso-pentane was found in the literature.
The degradation of CO during the transport is also found in the transatlantic transport. However, due to the high background concentrations of CO, the slope of the correlation between \( \ln(\text{CO}) \) and the residence times in reality is much smaller than the zero background condition. Thus in Fig. 5-12 the point representing CO falls to a place below the correlation line of hydrocarbons. This suggests that the involvement of compounds having high background concentrations can lead to overestimation of OH concentration and underestimation of the dilution rate. However, the influence is very small. It only leads an increase of 10% in the OH concentration, if CO is included. The uncertainty in the estimation is most possibly caused by the source distribution of hydrocarbons. Despite the different source profiles, the hydrocarbon concentrations can be well explained by the theory of the free tropospheric transport, probably because the influence of oxidation is larger than that of differences in the concentrations in the source regions.

In the transatlantic transport events, NO\(_x\) and NO\(_y\) concentrations had a large variation probably because of the effect of wet deposition on NO\(_y\) is very variable. However, ozone concentrations during the transatlantic transport are also found to have a surprisingly good correlation to the residence times (see Fig. 5-13). Yienger et al. (1999) suggested that ozone concentration has an increasing tendency in the free tropospheric transport in winter. The free tropospheric ozone formation rate at Jungfraujoch in spring was estimated to be about 0.7 ppb/d (Zanis et al., 2000). NO critical concentration for ozone destruction and formation in the free troposphere at Jungfraujoch was about 10 ppt in January (Zanis et al., 2000). In the photochemical steady states, NO concentration is about a half of the NO\(_2\) concentration. In the intercontinental transport events at Jungfraujoch, the average NO\(_x\) concentration was 60 ppt. The two points with the lowest NO\(_x\) concentrations (15 and 25 ppt respectively) also have the lowest ozone concentrations, suggesting that the ozone destruction could have already started. If these two points are excluded, the increasing rate of ozone is about 0.44 ppb/d from the linear correlation. The ozone formation in the free troposphere is consistent to the results of the previous literature. This on one hand shows that the air masses during the transatlantic transport events have similar source composition. On the other hand, it also
shows the availability of the trajectory approach (Pochanart et al., 2001 and 2003) under special conditions.

![Graph showing ozone concentration as a function of residence times in the free troposphere.](image)

**Fig. 5-13.** Ozone concentration as a function of the residence times in the free troposphere during the intercontinental transport. The red squares indicate cases with very low NOx concentrations (see text).

### 5.4.4 Dilutions in the local area and free troposphere

Figure 5-14 gives the correlations of ln(n-hexane/benzene) and ln(toluene/benzene) to ln(n-pentane/benzene) for all cases of the free tropospheric transport detected by the lowest toluene/benzene ratios. In the theory of photochemical degradation of hydrocarbons, the slope of the correlation is determined by the OH oxidation rates of the hydrocarbons (see Chapter 2.3). The slope of the correlation for n-hexane is close to the theoretical slope of 1.644 and the deviation from the theoretical line is determined by the dilution during transport. However, ln(toluene/benzene) has a negative correlation to ln(n-pentane/benzene) with $R^2$ of 0.3062. The deviation for toluene is most possibly determined by the dilution in the local area caused by local solvent evaporation. If the local toluene concentration is much higher than the toluene concentration from transport, but local concentration of other hydrocarbons is lower than or close to the concentration from transport, it is possible to get a negative correlation between toluene and other hydrocarbons. However, the source of local contribution is unclear.

The correlations between the logarithms of two hydrocarbon concentrations were also applied to estimate the dilution constant (refer to Eq. 2-7, in Chapter 2). The correlations in Table 5-4 are for the free tropospheric air from compact surface sources and all the free tropospheric air masses (11% in winter season with toluene/benzene smaller than 0.5, in the brackets), using n-pentane as the reference compound Y. The estimate of $K/L_Y$ (Y=n-pentane) with X of n-hexane, benzene and toluene yield dilution rates of 0.0046, 0.0050 and 0.0035 hour$^{-1}$, quite similar to the value presented above. However, the choices of reference hydrocarbon (Y) could lead to high deviations. For example, if the reference hydrocarbon is benzene, the
dilution rate is found to be about 0.0067 hour\(^{-1}\). So the first estimation (see Fig. 5-12) is more appropriate.

**Fig. 5-14.** Correlations between logarithms of the ratios of two pairs of hydrocarbons for all the free tropospheric cases found in October 2001 to January 2002.

**Table 5-4.** Correlations between logarithmic concentrations of n-pentane and other hydrocarbons in the free tropospheric air masses with surface origins. In brackets are the correlations for all the most aged free tropospheric air in Jungfraujoch. The poor correlations for toluene are probably caused by dilution in the local area.

<table>
<thead>
<tr>
<th>X</th>
<th>Slope</th>
<th>(R^2)</th>
<th>(K/L_{n\text{-pentane}})</th>
</tr>
</thead>
<tbody>
<tr>
<td>i-butane</td>
<td>0.6653</td>
<td>0.9448 (0.8925)</td>
<td>0.34</td>
</tr>
<tr>
<td>n-butane</td>
<td>0.9583</td>
<td>0.9055 (0.9383)</td>
<td>-</td>
</tr>
<tr>
<td>iso-pentane</td>
<td>0.9243</td>
<td>0.8789 (0.8637)</td>
<td>-</td>
</tr>
<tr>
<td>n-hexane</td>
<td>1.2468</td>
<td>0.9910 (0.9500)</td>
<td>0.74</td>
</tr>
<tr>
<td>benzene</td>
<td>0.6298</td>
<td>0.9290 (0.8902)</td>
<td>0.81</td>
</tr>
<tr>
<td>toluene</td>
<td>1.3777</td>
<td>0.6846 (0.1504)</td>
<td>0.56</td>
</tr>
</tbody>
</table>

In the dataset of all the free tropospheric air masses, all hydrocarbons have a good correlation to n-pentane on a logarithmic scale and the correlations are quite similar to those for the air masses with compact surface origins, except toluene (see values in the brackets in Table 5-4). This suggests that the source compositions of hydrocarbons are not much different from each other or are not important to the analysis. The dilution rate in the free troposphere in winter is very small (not only in the cases of compact surface sources), much smaller than the dilution rate, 0.016 hour\(^{-1}\) found by McKeen et al in PEM West A for summer conditions in 1992 (1996).

**5.5 Summary**
The behaviors of trace gases under the influence of the boundary layer in Jungfraujoch are complex. There have been several climatological studies at the mountain stations (Ingold et al., 2001; Zellweger et al., 2002), which have focused on the reactive nitrogen and aerosols. The climatology of these species is more closely related to the precipitation. The frontal influences on CO and hydrocarbons in the period of 16-30 April are also investigated in this chapter and a comparison between Jungfraujoch and Arosa is presented. The small scale (local thermal circulation) disturbance can be distinguished from the large scale disturbance (frontal lifting, mainly by cold fronts). It’s only during a cold frontal disturbance that the synoptic scale transport and mixing over the alpine region produces a similar background at Jungfraujoch and Arosa.

It should be noted that the frontal passages are of various types, primarily ana- and kata-fronts, determined by the motion of air masses (Barry and Chorley, 1999). The transport scale has to be determined by the frontal passage together with the trace gas concentrations. At Jungfraujoch, the air masses from synoptic scale transport (frontal lifting) have higher concentrations of the inert species, while the air masses from small scale transport have characteristics of emission in the “local” area. Foehn events, which are driven by the pressure gradient over the mountainous area, normally occur just before or after a frontal passage. Some of them go through the Po valley and carry up the polluted air masses. Others just flow at the heights around 2000 m asl above the Po basin (Seibert et al., 2000). So trace gas concentrations in foehn events have a large variation (Campana, 2003). It has to be noted that the air in foehn events is transported with less turbulence than in fronts. The trace gases at Arosa and Jungfraujoch during foehn events could have different sources. Campana (2003) detected a north foehn event, which happened just after the frontal passage over alpine region on November 23. The foehn air passed Jungfraujoch, but with no disturbance found at Arosa. The understanding of transport scales supports the weather classification of Zellweger et al. (2002).

The relationship between transport scales and trace gas behaviors is only applicable to the sites at the high altitude, like Jungfraujoch, where the background is the free troposphere. Conversely, Arosa is surrounded by the mountains, where the transport scale is not so pronounced, since the background was most of time more polluted. The weather influence can be studied by the classifications of the frontal days and fair weather days at Arosa.

In winter, the weather influence is more pronounced than in summer, because of the trapping effect of the persistent temperature inversion. Winter time trajectory analysis shows a positive correlation between ozone and residence time in Arosa in the clean background air, even though the inversion layer over the Swiss plateau entrapped the anthropogenic emissions (Fig. 5-5-2). The “leak” of the temperature inversions possibly contributes to the ozone increase with the residence time, which was more pronounced at Arosa than at Jungfraujoch. The different effects on the two stations are supported by the vertical gradient of NOx concentrations above the inversion layer. The shorter residence times of the frontal air, compared with those of the clean air, suggest that the hemispheric background ozone in winter could have been underestimated in Pochanart et al. (2001).

The trajectory analysis of the three cases at Jungfraujoch in Section 5.3.3 gives further evidence of the “leak” over the alpine mountains. The dilution in the lowermost free troposphere helps to explain the increase in ozone concentrations during the transport over Europe.
Although the trajectory approach described by Pochanart et al. (2001) is highly simplified and contains some uncertainties from the wind field and an incomplete understanding of the mixing process in the lower free troposphere, the analysis combined together with the chemical and meteorological feature provide a valuable method to study the contribution of European emission and intercontinental transport.

The largest scale transport at Jungfraujoch is found in the so called “undisturbed free troposphere”, in which intercontinental transport and stratospheric intrusion found at Jungfraujoch could be detected by the most aged air masses (indicated by hydrocarbon ratios) and by the simultaneous decrease of relative humidity, see Section 5.4. However, stratospheric intrusion events are not included in the analysis, because they normally arrive with strong turbulent mixing.

The most aged air masses found at Jungfraujoch have the characteristics of hemispheric background, and several air masses in the winter 2001 have been encountered after the transatlantic transports through warm conveyer belts. During the transatlantic transports hydrocarbons degrade primarily through OH oxidation. The OH concentration is estimated through hydrocarbon concentrations to be about $5.1 \times 10^5 \text{ cm}^{-3} \text{ s}^{-1}$.

If the free tropospheric air is thought of as the air masses without any European contribution, such air can rarely be found at Arosa under the influence of thermal lifting. In the 11% free tropospheric cases at Jungfraujoch found in winter, the influence of local contamination was also identified in case of toluene.
6 Comparison between ECMWF and aLMo trajectories

6.1 Introduction

Trajectories are widely used to identify sources of air masses (Stohl, 1996; Yonemura, 1999) and to explain the concentrations of trace gases (Pochanart et al., 2001; Lobert and Harris, 2002). They are also used in Lagrangian chemical models (Derwent et al., 1991). There are many kinds of trajectories with different calculation processes and different wind fields. It was suggested that three-dimensional trajectories are more accurate than isentroptic and isosigma trajectories in the boundary layer (Stohl, 1998). However, the three-dimensional trajectories are still not very accurate for the description of the transport in the planetary boundary layer. It was suggested more accurate trajectory model, taking into account turbulence, be developed for the study of transport in the planetary boundary layer and over the complex topography (Stohl, 1998). However, calculations for complicated trajectories are rather time consuming and they are not considered here.

ECMWF and aLMo trajectories are two widely used three-dimensional trajectories in Switzerland. ECMWF trajectories are believed to be suitable tools to study the long range transport (Wernli and Davies, 1997). aLMo trajectories were recently developed by MeteoSwiss and have been used for the detection of fronts at Jungfraujoch (Forrer et al., 2000). However, it is unknown which trajectories are more accurate.

Stohl et al. (2001) compared three 3-D ECMWF trajectories calculated by different tools, LAGRANTO, TRAJKS and FLEXTRA and found that the trajectories have a good agreement with deviations smaller than 10%. Thus the difference between the two trajectory calculation methods (LAGRANTO and TRAJEK-DWD) seems less important. The differences are determined more by the wind fields of the ECMWF and aLMo models. The different wind fields are shown in Table 6-1. aLMo wind field has a higher resolution. However, the only aLMo trajectories available in the present are based on the forecast wind field. The annual mean surface pressure of Jungfraujoch is 728 hPa in aLMo and 816 hPa in ECMWF.

<table>
<thead>
<tr>
<th>Table 6-1. Difference between ECMWF and aLMo wind field</th>
</tr>
</thead>
<tbody>
<tr>
<td>Data</td>
</tr>
<tr>
<td>----------------</td>
</tr>
<tr>
<td>ECMWF analysis</td>
</tr>
<tr>
<td>aLMo forecast</td>
</tr>
</tbody>
</table>
In this chapter, the two types of trajectories are compared. Most of the chemical tracers used to study the accuracy of trajectories are inert species, but they are used mainly at the places with simple source distributions (Zeng et al., 2003) or released artificially and specifically (Stohl, 1998). At Jungfraujoch, where there are frequent influences of the anthropogenic activities in the alpine valleys and Swiss plateau, the ECMWF and aLMo trajectories are compared based on the trace gas concentrations. We first make a statistical comparison of the spatial divergence of the trajectories based on synoptic weather types of AWS (Alpine Weather Statistics). Then the trace gas concentrations are statistically compared to the altitudes of two trajectory systems. The trace gas concentrations at Jungfraujoch in lifting cases, indicated by the altitudes of trajectories, are also compared. At the end, the reliabilities of the trajectories are further discussed, based on case studies.

6.2 Trajectories

ECMWF trajectories are calculated 6 days backward every 4 hours (0000, 0400, 0800, 1200, 1600 and 2000 UTC) for the Jungfraujoch measurement station (46.55°N, 7.98°E), at 11 vertical levels (630, 650, 670, 690, 710, 730, 750, 770, 790, 810, 830 and 850 hPa) by the trajectory calculation tool, LAGRANTO (Wernli and Davies, 1997). aLMo trajectories are calculated by the TRAJEK-DWD model at two altitudes, 700 hPa and 100 m over ground for Jungfraujoch every 4 hours, supplied by Daniel Schaub, EMPA. Due to the constraint of the model domain, aLMo trajectories are calculated only up to 48 hours backward. Some trajectories are lost because of the choice of criteria or the problem of leaving the domain.

For the comparison, the ECMWF trajectories and the aLMo trajectories are calculated for September 2001 to August 2002.

6.3 Statistical comparison based on AWS weather types

Table 6-2 gives an overview of the distribution of the days in the AWS weather classes and the distributions of frontal days and all the cold and weak fronts. About one third of the days in the whole year are of northerly advection. The cold fronts normally arrive at Jungfraujoch by fast northerly advection. 110 days of frontal passage and 62 days of cold front passage occurred between September 2001 and August 2002. It was found that frontal days occurred most readily in the weather types 2, 3, 4, 5 and 6, and the probabilities of frontal passage (frontal days/all days in the weather type) are highest in weather types 3, 4, 5, 8, among which the probability of cold fronts is highest for weather types 3, 4, 8.

The comparison between the aLMo trajectories and the ECMWF trajectories is first performed based on two parameters: the mean horizontal distances \( Dist \) and pressure differences \( P_{\text{diff}} \) between the ECMWF and the aLMo trajectories over the previous \( N \) hours:

\[
Dist = \frac{1}{N} \sum_{i=1}^{N} \| (x, y)_{ECMWF} - (x, y)_{aLMo} \| ,
\]

\[
P_{\text{diff}} = \frac{1}{N} \sum_{i=1}^{N} (P_{ECMWF} - P_{aLMo}) .
\]

(6-1)

(6-2)
The means of 24 hours backward Dist and \( P_{\text{diff}} \) are applied for the comparison (\( N=24 \)). The two parameters are calculated between all ECMWF trajectories at all altitudes (650, \( \ldots \), 790 and 810 hPa) and the aLMo trajectories. The values of \( P_{\text{diff}} \) show a normal distribution and those of Dist give a one-tailed distribution at the high value side. Thus we compared the Dist on a logarithmic scale.

**Table 6-2.** Weather types of AWS in September 2001 to August 2002

<table>
<thead>
<tr>
<th>Basic</th>
<th>Extend type</th>
<th>All Days</th>
<th>All frontal days</th>
<th>Cold frontal days</th>
</tr>
</thead>
<tbody>
<tr>
<td>Advective</td>
<td>1. Easterly</td>
<td>8</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td></td>
<td>2. Southerly</td>
<td>27</td>
<td>10</td>
<td>4</td>
</tr>
<tr>
<td></td>
<td>3. Westerly</td>
<td>31</td>
<td>14</td>
<td>12</td>
</tr>
<tr>
<td></td>
<td>4. Northerly</td>
<td>49</td>
<td>32</td>
<td>26</td>
</tr>
<tr>
<td>Convective</td>
<td>5. Cyclonic</td>
<td>26</td>
<td>15</td>
<td>3</td>
</tr>
<tr>
<td></td>
<td>6. Indifferent</td>
<td>127</td>
<td>28</td>
<td>11</td>
</tr>
<tr>
<td></td>
<td>7. Anticyclonic</td>
<td>22</td>
<td>2</td>
<td>0</td>
</tr>
<tr>
<td>Mixed</td>
<td>8. Mixed</td>
<td>18</td>
<td>8</td>
<td>5</td>
</tr>
<tr>
<td>Total</td>
<td></td>
<td>365</td>
<td>110</td>
<td>62</td>
</tr>
</tbody>
</table>

Figure 6-1 gives the means of \( P_{\text{diff}} \) and ln(Dist). The mean altitude of the 24 hours backward ECMWF trajectories for starting height 770 hPa (770 hPa ECMWF trajectories in the following paragraph) is most similar to the mean altitude of the aLMo trajectories for starting height 700 hPa (700 hPa aLMo trajectories). The horizontal distance between these two trajectories is also the smallest, compared with all the other ECMWF trajectories. The starting heights of the 770 hPa ECMWF trajectories and the 700 hPa aLMo trajectories are individually about 40 and 20 hPa over the grid surface in both wind fields.

It is interesting to see that both of the parameters showed dependence on AWS weather types. In the westerly advection (3), northerly advection (4) and mixed types (8), the aLMo trajectories are much lower than the ECMWF trajectories. The trajectory difference depends on the transport velocity (Personal communication with H. Wernli). Since the northerly and westerly advection normally have characteristics of higher wind speed than under other weather conditions, the disagreements between these two trajectories could be larger in the long range transport.

The deviations (\( P_{\text{diff}} \) and ln(Dist)) between the two trajectories in frontal days and cold frontal days (see Fig. 6-1) are a little bit higher than those for the mean of all trajectories, but still smaller than those for northerly advectons. The lower altitudes of the aLMo trajectories compared with the ECMWF trajectories are more closely related to the synoptic weather types. In the group of cold frontal days, there are some days with prevailing southerly wind. Excluding these day, the \( P_{\text{diff}} \) and ln(Dist) of cold fronts from the northerly are similar to those in the northerly advection types (“north cold” in Fig. 6-1).
6. COMPARISON BETWEEN ECMWF AND ALMO TRAJECTORIES

Fig. 6-1-1 Mean logarithmic values of $\ln(Dist)$ (Dist has the unit of km) between the ECMWF trajectories and 700hPa aLMo trajectories, categorized by the days of different weather types. The x-axis shows arriving altitudes of the ECMWF trajectories while the dashed lines show the corresponding Dist values in different AWS weather types, the solid line with filled diamonds shows the results of all 365 days and the solid lines with blank diamonds, blank rectangles and blank triangles are the means of all fronts (cold and weak fronts), cold fronts, and the northerly cold fronts. 650, …, 790 and 810 are representative for the 650 hPa, …, 790 hPa and 810 hPa ECMWF trajectories.

Fig. 6-1-2 The means of the values of $P_{diff}$ between the ECMWF trajectories and 700 hPa aLMo trajectories, categorized by the days of different weather types. The lines with different signals have the same meaning as in Fig. 6-1-1.

6.4 Relations between heights of trajectories and the trace gas concentrations
It is not possible to judge the reliability of trajectories only with the two parameters in the last section, thus we compare the altitudes of trajectories with the trace gas concentrations at Jungfraujoch. For this purpose, we considered the mean altitude (hPa) of the ECMWF and the aLMo trajectories 24 hours prior to their arrival at Jungfraujoch, which is called the mean altitude in this section. Normally there should be a correlation between trace gas concentrations and the altitude of trajectories. However, the correlation is obscured because of the complication of transport (Chapter 5) and it is not clear which compound has better relation to the boundary layer influence. An investigation on the correlations between the altitude of trajectories and concentrations of all the trace gases helps us to learn: i) which compounds can reflect the boundary layer influence at Jungfraujoch, ii) at which arrival altitude, ECMWF trajectories are more reliable in showing the boundary layer influence and iii) which trajectories are more accurate, ECMWF or aLMo trajectories.

The correlations between trace gas concentrations and 24 hour backward altitudes (hPa) of trajectories are generally very weak (Table 6-3). The correlations in winter are better than in summer, in which, toluene and ln(toluene/benzene) (ln(T/B) in Table 6-3) have the best correlations with the altitude of ECMWF trajectories. The correlation coefficients are higher for the ECMWF trajectories of lower arriving altitude. The correlations for the aLMo trajectories are much worse compared with those for the ECMWF trajectories, suggesting that aLMo trajectories are not more accurate than ECMWF trajectories concerning the description of the lifting of air masses at Jungfraujoch, although the resolution of the DWD wind field is higher. This might be caused by the use of forecast data in aLMo trajectories.

**Table 6-3** Correlation coefficients (r) between chemical parameters, including trace gas concentrations and ln(toluene/benzene) and NOx/NOy, and the mean altitude of trajectories (hPa) in the previous 24 hours before arriving at Jungfraujoch. Each correlation contains at least 300 points. The correlation coefficients higher than 0.25 are highlighted. 650,...,790 and 810 – 650 hPa, ..., 790 hPa and 810 hPa ECMWF trajectories; lm700 and lm100 – aLMo trajectories with starting point at 700 hPa and 100 m over ground. w – winter; s – spring.

<table>
<thead>
<tr>
<th></th>
<th>650</th>
<th>670</th>
<th>690</th>
<th>710</th>
<th>730</th>
<th>750</th>
<th>770</th>
<th>790</th>
<th>810</th>
<th>lm700</th>
<th>lm100</th>
</tr>
</thead>
<tbody>
<tr>
<td>w</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
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<tr>
<td>CO</td>
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<td>0.161</td>
<td>0.185</td>
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<td>0.252</td>
<td>0.273</td>
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<td>0.277</td>
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<td>0.308</td>
<td>0.321</td>
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<tr>
<td>ln(T/B)</td>
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<td>0.435</td>
<td>0.437</td>
<td>0.433</td>
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<td>0.091</td>
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<tbody>
<tr>
<td>CO</td>
<td>0.164</td>
<td>0.159</td>
<td>0.161</td>
<td>0.169</td>
<td>0.169</td>
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<td>0.165</td>
<td>0.138</td>
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<tr>
<td>NOx</td>
<td>0.207</td>
<td>0.211</td>
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<td>0.246</td>
<td>0.238</td>
<td>0.219</td>
<td>0.204</td>
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</tr>
<tr>
<td>NOx/NOy</td>
<td>0.096</td>
<td>0.096</td>
<td>0.079</td>
<td>0.065</td>
<td>0.047</td>
<td>0.029</td>
<td>0.011</td>
<td>0.004</td>
<td>0.044</td>
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<td>0.243</td>
</tr>
<tr>
<td>NOy</td>
<td>0.215</td>
<td>0.220</td>
<td>0.244</td>
<td>0.288</td>
<td>0.294</td>
<td>0.289</td>
<td>0.293</td>
<td>0.271</td>
<td>0.198</td>
<td>0.047</td>
<td>0.010</td>
</tr>
<tr>
<td>benzene</td>
<td>0.274</td>
<td>0.283</td>
<td>0.296</td>
<td>0.301</td>
<td>0.295</td>
<td>0.326</td>
<td>0.354</td>
<td>0.358</td>
<td>0.361</td>
<td>0.298</td>
<td>0.283</td>
</tr>
<tr>
<td>ln(T/B)</td>
<td>0.155</td>
<td>0.155</td>
<td>0.161</td>
<td>0.169</td>
<td>0.200</td>
<td>0.237</td>
<td>0.259</td>
<td>0.205</td>
<td>0.093</td>
<td>-0.045</td>
<td>-0.119</td>
</tr>
<tr>
<td>toluene</td>
<td>0.156</td>
<td>0.159</td>
<td>0.171</td>
<td>0.177</td>
<td>0.186</td>
<td>0.207</td>
<td>0.250</td>
<td>0.233</td>
<td>0.203</td>
<td>0.089</td>
<td>0.031</td>
</tr>
</tbody>
</table>
In summer, most of the parameters have better correlations to the altitudes of the ECMWF trajectories than those to the altitudes of the aLMo trajectories, except NO\textsubscript{x} concentrations. The best correlations for the ECMWF trajectories are found in the group of the 770 hPa ECMWF trajectories. Among all the chemical parameters, benzene has better correlations than any other compound. One reason is the higher oxidization rate in summer, so that toluene and NO\textsubscript{x} has been partially oxidized even in the thermal lifting before arriving. The other reason is that the altitudes of trajectories are more closely related to the frontal passage, which has a longer path. In fact, the height over ground (\textit{HOG}, hPa) is better in showing the influence of boundary layer emission. \textit{HOGs} have better correlations to the ln(toluene/benzene) for the ECMWF trajectories, as discussed in Appendix C. For the height over ground (corresponding to the boundary layer influence), better correlation is found for ln(toluene/benzene). The better correlation between NO\textsubscript{x} concentrations and altitudes of the aLMo trajectories are possibly due to the lightning during frontal passages, since the altitudes of the aLMo trajectories are highly related to the weather conditions. In the following sections we will make a comparison between the lifting cases detected by the altitude of the ECMWF and aLMo trajectories.

6.5 Study on the lifting cases detected by trajectories

Cold fronts normally lead to large scale lifting, which could transport aged air masses with a smaller toluene/benzene ratio to Jungfraujoch in summer. However, the very weak front passage can hardly lead to the large scale lifting. As shown in Fig. 5-1, on 24-25 April, the variations of trace gases are quite similar to the variations in the indifferent convective days, on which the air masses are from the closest sources.

The percentage of days classified as the “cold frontal passage” in each season going from autumn 2001 to summer 2002, were of 18\%, 21\%, 10\% and 20\%. Figure 6-4 gives the seasonal medians and the corresponding cold frontal medians of four chemical parameters. The cold fronts coming from the south is not included, since the northerly cold fronts are related more to the weather type 4 and the south-originating fronts could carry the polluted air masses from the Po valley. The concentrations in the north-originating cold fronts are generally higher than the seasonal median, especially for the short lived compounds, NO\textsubscript{x} and NO\textsubscript{y}. However, a lower toluene/benzene ratio is found in summer during the front passages because the regional background during frontal passages is oxidized.

The trace gas concentrations in the air masses from the lowest altitude detected by the ECMWF and aLMo trajectories are compared together with the seasonal median concentrations. The lifting cases are selected by the lowest trajectories at the same percentage of cold frontal days in different seasons, as described in the last paragraph. The 770 hPa ECMWF trajectories are used to make the comparison, since their altitudes are closest to lm700 trajectories. The air masses from both the lowest ECMWF and aLMo trajectories (see Fig. 6-4) have higher values of primary pollutant concentrations than the seasonal median, suggesting that both trajectories are suitable for describing the boundary layer influence. However, a pronounced difference between the two trajectories is found in summer. The ratios of tolu-
ene/benzene from the lowest aLMo trajectories are much lower than the summer median. The difference in summer could be explained by the trace gas behaviors in the frontal passages, especially the cold frontal passages. The lower toluene/benzene ratio and higher primary pollutant concentrations seem to be (to some extent) characteristic of cold fronts, as discussed in Chapter 5. The aLMo trajectories have lower altitude in the weather types of 3, 4, 8 and the primary distribution of cold fronts are found in the weather types of 3, 4 and 8. The previous version of aLMo trajectories, SM trajectories, has been used for the detection of frontal liftings by Zellweger et al. (2002). In the lifting cases detected by the ECMWF trajectories, air masses have much high toluene/benzene ratios. ECMWF trajectories are not so strongly related to the cold frontal passage and the local boundary layer influence with fresh emission can possibly also be found by inspecting the lowest proportion of ECMWF trajectories.

**Fig. 6-4.** The mixing ratios of primary pollutants and the ratios of toluene/benzene in the air masses from the lowest altitude, shown by the 770 hPa ECMWF trajectories and the aLMo trajectories. The seasonal medians and the medians during frontal passages are also included in the figure (the solid and dashed lines).

### 6.6 Case studies for comparison between ECMWF and aLMo trajectories

In this section, two case studies are performed to show the difference between ECMWF and aLMo trajectories: i) The 13-15 November was a case of very high primary pollutant concentrations in winter; ii) The 27 to 30 June was a case with persistent weather and very
high toluene/benzene ratios. The AWS weather types of the days in the two periods are listed in Table 6-4.

The 710, 730 and 750 hPa ECMWF trajectories are selected for the comparison with aLMo trajectories, because the ECMWF trajectories for the three selected levels showed clearly a dependence of the transport paths on the arrival altitudes.

Table 6-4. Synoptic weather types of two periods in 2001 -2002

<table>
<thead>
<tr>
<th>AWS Weather types</th>
<th>AWS Weather types</th>
</tr>
</thead>
<tbody>
<tr>
<td>Nov 12, 01</td>
<td>8</td>
</tr>
<tr>
<td>Nov 13, 01</td>
<td>4</td>
</tr>
<tr>
<td>Nov 14, 01</td>
<td>2</td>
</tr>
<tr>
<td>Nov 15, 01</td>
<td>6</td>
</tr>
<tr>
<td>June 27, 01</td>
<td>6</td>
</tr>
<tr>
<td>June 28, 01</td>
<td>3</td>
</tr>
<tr>
<td>June 29, 01</td>
<td>6</td>
</tr>
<tr>
<td>June 30, 01</td>
<td>6</td>
</tr>
</tbody>
</table>

6.6.1 Winter case

At midnight of 13-14 November 2001, a cold front was present at the Jungfraujoch measurement station together with very high concentrations of primary pollutants. The same front was also present at Arosa on the nights of 13 and 14 November 2001 (see Fig. 6-5). After the frontal passage, the direction of the wind changed from northerly to southerly in the morning of 14 November. The second peaks of trace gas concentrations were monitored together with southerly wind at midnight of 14-15 November at Jungfraujoch. The ECMWF and aLMo trajectories have good coherence during the cold front passage at midnight of 13-14 November. However, a large deviation is found in the second disturbance. The ECMWF trajectories indicate advection from the lower altitude of south of the Alps, but the aLMo trajectories showed that the air masses were from the east alpine region and the air masses were over Arosa and Davos 12 hours earlier. Campana (2003) made a comparison between the concentrations of CO and NO\textsubscript{y} at Jungfraujoch, at midnight of 14-15 November, and at Arosa and Davos, at 1200 CET on 14 November, and found similar concentrations (NO\textsubscript{y}: 9.4 ppb at Jungfraujoch, 7.0 ppb at Arosa). However, the transport without dilution is difficult to explain. In addition, the fact that the aLMo trajectories for the same time period do not originate from the surface provides evidence against the explanation of the polluted events suggested by the aLMo trajectories. The transport path indicated by ECMWF trajectories is more reasonable in this case.

After the second disturbance of lifting, the relative humidity dropped sharply and both trajectories showed the downward transport of the air masses.
Fig. 6-5. Trace gas concentrations and meteorological conditions at Jungfraujoch on 12-17 November 2001. NOx/NOy and toluene/benzene are also included.
6. COMPARISON BETWEEN ECMWF AND ALMO TRAJECTORIES

Fig. 6-6. Comparison of trajectories of ECMWF (710hp, 730hp and 750hp), aLMo 100 and aLMo 700 on 13-15 November 2001. Every figure provides the five trajectories of particular time. Color scales describe the altitudes (hPa) of trajectories.
6.6.2 Summer case

From 27 June to 30 June, all the days were of the indifferent convective weather type (class of AWS), except 28 June, which was a case of the westerly advection. A weak front (see Fig. 6-7) came in the afternoon of 28 June with lower toluene/benzene ratios and enhanced concentrations of primary pollutants. Lower concentrations were found on other days, but with higher toluene/benzene ratios. After 1 July, the wind direction changed and the southerly advection prevailed together with enhanced concentrations of all the primary pollutants.

![Graph showing meteorological conditions and trace gas concentrations from June 27 to July 1, 2002.](image)

**Fig. 6-7.** Trace gas concentrations and meteorological conditions at Jungfraujoch on June 27-July 1st 2002. NOx/NOy and ln(toluene/benzene) are also included.
Fig. 6-8. Comparison of trajectories of ECMWF (710hPa, 730hPa and 750hPa), aLMo 100 and aLMo 700 on 28 June to 30 June. The arrows show the aLMo trajectories. Every figure provides the five trajectories of particular time. Color scales describe the altitudes (hPa) of trajectories.
The investigation is focused on the trajectories of 27 to 30 June. When the weak front arrived on 28 June (see 1200 UTC trajectories in Fig. 6-7), both the 700 hPa aLMo and 100 m aLMo trajectories were from very low altitudes. However, the ECMWF trajectories are highly dependent on the arrival altitude. The 750 hPa ECMWF trajectory is close to the path of aLMo trajectories and 770 hPa ECMWF trajectory is even closer to the aLMo trajectories (not shown in the Fig. 6-8). In this case both trajectories are reliable, although the horizontal disagreement is large between the 710 and 730 hPa ECMWF and aLMo trajectories. The behavior of the ECMWF trajectories in this event also shows that the lower ECMWF trajectories can give a better description of the boundary layer influence.

On 30 June, the aLMo trajectories were higher than the 750 and 730 hPa ECMWF trajectories but lower than the 710 hPa trajectory. The convergence of the ECMWF trajectories arriving at the different altitudes probably gives more reliable flow patterns, considering the air masses of higher toluene/benzene ratios on 30 June.

6.7 Conclusions

The ECMWF and aLMo trajectories are compared in this chapter, which provides a further understanding of the characteristics of the two trajectories. The 770 hPa ECMWF trajectories are closest to the 700 hPa aLMo trajectories on average. The largest difference between ECMWF and aLMo trajectories is found under the AWS weather type of northerly advection. Better correlations between the chemical parameters and the altitude of trajectories are found for the ECMWF trajectories, though both trajectories can describe the lifting cases. In both the lifting cases identified by the 770 hPa ECMWF trajectories and also by the aLMo trajectories, higher primary pollutant concentrations are detected. However, the toluene/benzene ratios are very low in the lifting cases found by aLMo trajectories. This indicates that the lifting cases found by the aLMo trajectories are mostly due to the cold frontal passage. The ECMWF trajectories seem to be capable to show the boundary layer influence in the convective days.

In two case studies the performance of two trajectories are compared to the frontal and convective disturbance. Most of time, the ECMWF and aLMo trajectories are in reasonable agreement. In a few cases, there are large differences between two trajectories. ECMWF trajectories seem more reliable in showing the boundary layer influence in comparison to aLMo trajectories, especially during the convective weather days, when the air masses are transported in a small scale as discussed in Chapter 5. Stunder et al. (1996) compared trajectories calculated from forecast data and those calculated from reanalysis data, both from NCEP Nested Grid Model (NGM), and found that the forecast trajectories are less accurate in the high pressure system. The poor performance of aLMo trajectories under convective weather conditions could also originate from the forecast wind field. Further comparison for the reanalysis aLMo trajectories has yet to be considered. The case studies also suggest that the trajectories arriving at an altitude closer to the model surface are, among all ECMWF trajectories, more representative of the boundary layer influence.
Although the forecast aLMo trajectories are not very accurate in showing all the lifting cases, they are reasonably suitable for the detection of the frontal lifting cases, as Zellweger et al. (2002) suggested, in the perspective of transport scales (see Chapter 5).
7 Summertime measurements at Arosa and comparison with simulations by a chemical trajectory box model

7.1 Introduction

Pochanart et al. (2001) reported a surprisingly good correlation between the ozone concentrations at Arosa and the residence times of the air masses over Europe in summer. However, weather conditions (see Section 5.3), the spatial distribution of European emission (e.g. foehn events as described by Campana et al., 2004) and even the variation of the hemispheric background (see Section 5.3) can lead to deviations, which cannot be described by the simple approach used by Pochanart et al. (2001). In this chapter, data analysis of measurements in summer, 2002 is presented and the contribution of European emission is simulated by a chemical trajectory box model, based on the assumption that the hemispheric background concentrations of ozone and its precursors are constant.

Lagrangian models only provide a realistic description if turbulent mixing can be ignored, for example at higher altitudes in the atmosphere (Sparling et al., 1995). However, in consideration of the computer resources required, Lagrangian photochemical models are still in use for long term simulations in the case of complicated reactions (Stohl, 1998). Since the emission in the planetary boundary layer is mixed turbulent into the upper layer (the so-called residual layer) errors cannot be avoided in this model. We aim to use the trajectory chemical box model to attest the availability of the statistical trajectory approach by Pochanart et al. (2001).

7.2 Chemical trajectory box model

7.2.1 Basic approach

The basic mechanism is described by the following equation:

\[
\frac{dC_i}{dt} = P_i + D\left(\frac{E_i}{h} - \frac{C_i}{h} \cdot V_d - (C_i - B_i) \frac{1}{h} \frac{dh}{dt}\right),
\]

where

- \( C_i \) is the concentration of the \( i \)th compound,
- \( P_i \) is the photochemical production or loss of the \( i \)th compound,
- \( D \) describes the mixing with the boundary layer (\( D \) is 0 or 1),
- \( E_i \) is the emission rate from EMEP,
7. SIMULATIONS BY A CHEMICAL BOX MODEL

$h$ is the boundary layer height, $V_d$ is the deposition rate, and $B_i$ is the concentration in the free troposphere.

The concentration of each compound is determined by the photochemical transformation $(P_i)$, the emission $(\frac{E_i}{h})$, the deposition $(\frac{C_i}{h} \cdot V_d)$ and the exchange between the residual layer and the boundary layer $((C_i - B_i) \frac{1}{h} \frac{dh}{dt})$. Figure 7-1 shows an overview of the modeling approach. In the residual layer ($D = 0$), the concentrations in the air parcel are only determined by the photochemistry. In the case where the air parcel is transported in the boundary layer ($D=1$, the air parcel is lower than ECMWF boundary layer height), emission and deposition occur in the box. The air masses in the boundary layer are diluted during the development of the boundary layer height. The background concentration $(B_i)$ is considered as constant in the model, as set by the initial concentrations. In the simulation, only the background concentrations of CO, NO$_x$, and ozone are considered.

The ECMWF boundary layer heights are estimated by the forecast at 0000 and 1200 UTC and have a time resolution of 3 hours. The data of 1 hour resolution are obtained by linear interpolation. When the boundary layer height is lower than 200 meters, no mixing is considered in the model. This is in order to avoid the large amounts of emission input and to limit the uncertainties caused by the spatial resolution of the ECMWF model.

Two simulation procedures are applied, considering the five-trajectory ensemble (see Table 7-1). In the simulation with five individual trajectories (model II), trace gas concentrations are calculated as the averages of five simulations at the receptor place, Arosa. The comparison between the two modules is discussed in Section 7.4.

Table 7-1. Simulations with different procedures.

<table>
<thead>
<tr>
<th>model description</th>
<th>Concentrations are simulated with the average trajectory of the five-trajectory ensemble</th>
<th>Concentrations are the averages of five simulations upon the individual trajectories</th>
</tr>
</thead>
<tbody>
<tr>
<td>I</td>
<td>Concentrations are simulated with the average trajectory of the five-trajectory ensemble</td>
<td>Concentrations are the averages of five simulations upon the individual trajectories</td>
</tr>
<tr>
<td>II</td>
<td>Concentrations are the averages of five simulations upon the individual trajectories</td>
<td></td>
</tr>
</tbody>
</table>

7.2.2 Chemical mechanism

A photochemical trajectory box model, developed by Max Planck Institute, Mainz, is applied to the simulations. A detailed description can be found in Crutzen et al. (1992) and Müller et al. (1994). The model is written in the code of FASCIUMILE. The in-situ solar radiation is calculated by the zenith angle based on the ozone absorption and the Rayleigh scattering in the upper atmosphere. The concept of the box model is shown in Fig. 7-1. In the simulation, cloud and aerosol influences are not considered, because of the complication of their influence on the radiation and photolysis rates. In addition, the dynamic mixing process during frontal transport is also complicated, which restricts the accuracy of the simulation. So the simulation is only appropriate for days under good weather conditions.
The trajectory box model was extended by non-methane organic chemistry. The hydrocarbon oxidation mechanism is taken from MCM3 (Master Chemical Mechanism), which is also a FACSIMILE model and is easily integrated into the box model. All the photolysis rates are calculated based on their relations to the photolysis rate of CH$_3$OH, which is included in the Mainz photochemical box model. Considering the limited space of the model, only 8 hydrocarbons, namely ethane, propane, n-butane, n-hexane, ethene, propene, benzene and toluene, are included and the mechanism is simplified according to the paper of Derwent et al. (1996). The simplifications include: (1) Oxidations of ethene and propene by NO$_3$, and oxidations of other hydrocarbons by O$_3$ and NO$_3$, are excluded. (2) Since organic peroxy radicals primarily react with nitric oxide and methyl peroxy radicals, reactions of organic peroxy radicals with HO$_2$ and other peroxy radicals are omitted. The mechanism of the reactions of benzene and toluene oxidation is not simplified because the reactions of aromatic hydrocarbons are very complicated and not yet completely known.

EMEP emission

Initial concentrations of ozone, NO$_x$ and hydrocarbons

Trajectories

Ozone soundings

Trajectory box model – trajbox.fac (Mainz)
MCM3

Fig. 7-1. Diagram of the trajectory box model simulation.

7.2.3 Trajectories and the input of EMEP emissions

The trajectories integrated in the model are 10 days 3-dimensional backward trajectories based on the ECMWF wind field (Wernli and Davies, 1997). Five trajectories are calculated for air masses reaching the receptor site (Arosa, 800 hPa), one in center and four each displaced by 0.5 degree. The time resolution of ECMWF trajectories is 6 hours. When they are applied to the box model, more points are linearly interpolated onto the trajectories, giving a time step of one hour in the model. Corresponding to the assumption that the ozone concentrations are constant over the Atlantic Ocean, the trajectories were cut at 0000 UTC just before entering the European range determined by the land-sea mask. Only the 0600 UTC trajectories at Arosa are considered in the simulations, taking into account the complex flow pattern in the daytime. Since the background is thought of as air masses over the North Atlantic, the trajectories are initialized at the time 0000 UTC before they cross the European land sea mask. Nine days of residence over Europe is considered as the upper limits in the simulation.

The EMEP 50×50 km$^2$ grid emissions of CO, NO$_x$ as NO$_2$ and non-methane volatile organic compounds (NMVOC) are integrated into the model along the trajectories. The domain
of EMEP is shown in Fig. 7-2, in which the trajectory of air masses on 20 June 2002 is included. The non-methane hydrocarbons are considered to be comprised of 8 hydrocarbons, proportioned according to the UK hydrocarbon emission inventory of 1987: C₂H₆: 6.15%, C₃H₈: 1.47%, n-C₄H₁₀: 27.9%, n-C₆H₁₄: 7.10%, C₂H₄: 10.88%, C₃H₆: 3.93%, C₆H₆: 8.04% and C₇H₁₀: 34.53% percentage by mass (Derwent et al., 1991). Since all hydrocarbons are considered to be comprised of the 8 species, the simulations of the individual hydrocarbon concentrations in the air masses arriving at Arosa are not compared with measurements of the individual hydrocarbons at Arosa.

![Fig. 7-2. 10 days backward trajectories of 19 June (yellow lines) and the EMEP NOₓ emission (as NO₂ kton/y) in 2000.](image)

### 7.2.4 Depositions and initial concentrations

Since cloud influence is not included, only the dry deposition is considered in the model. Annual dry deposition rates over land (Table 7-2) from von Kuhlmann (2001) are used for most of species. The deposition rates of H₂O₂ and HNO₃ are from Plummer et al. (1996).

Ozone concentration is initialized by the background estimated by the trajectory approach by Pochanart et al. (2002). H₂ and CH₄ values are initialized according to Yienger et al. (1997). The initialization of concentrations of other species is based on the median value at Jungfraujoch (data from EMPA), and C₂ and C₃ hydrocarbons are initialized according to the summer background of hydrocarbon ratios over the North Atlantic (Penkett et al., 1993).
Table 7-2. Dry deposition rates and initial concentrations used in the model

<table>
<thead>
<tr>
<th>Species</th>
<th>$V_d$ [cm/s]</th>
<th>Initial concentrations $^1$</th>
</tr>
</thead>
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<td>0.26</td>
<td>42 ppb</td>
</tr>
<tr>
<td>CH$_2$O</td>
<td>0.36</td>
<td>25 ppt</td>
</tr>
<tr>
<td>CO</td>
<td>0.01</td>
<td>123 ppb</td>
</tr>
<tr>
<td>H$_2$O$_2$</td>
<td>0.60</td>
<td>-</td>
</tr>
<tr>
<td>NO$_x$ as NO$_2$</td>
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<td>10 ppt</td>
</tr>
<tr>
<td>HNO$_3$</td>
<td>1.0</td>
<td>300 ppt$^2$</td>
</tr>
<tr>
<td>CH$_3$OH</td>
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<td>-</td>
</tr>
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<td>CH$_3$O$_2$H</td>
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<td>-</td>
</tr>
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<td>150 ppt</td>
</tr>
<tr>
<td>CH$_3$CHO</td>
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<td>-</td>
</tr>
<tr>
<td>CH$_3$CO$_2$H</td>
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</tr>
<tr>
<td>CH$_3$COCH$_3$</td>
<td>0.08</td>
<td>-</td>
</tr>
<tr>
<td>CH$_4$</td>
<td>-</td>
<td>1.75 ppm$^3$</td>
</tr>
<tr>
<td>H$_2$</td>
<td>-</td>
<td>0.50 ppm$^3$</td>
</tr>
<tr>
<td>H$_2$O</td>
<td>-</td>
<td>2.14 g/kg</td>
</tr>
<tr>
<td>ethane</td>
<td>-</td>
<td>1150 ppt</td>
</tr>
<tr>
<td>propane</td>
<td>-</td>
<td>90 ppt</td>
</tr>
<tr>
<td>n-butane</td>
<td>-</td>
<td>40 ppt</td>
</tr>
<tr>
<td>ethene</td>
<td>-</td>
<td>1000 ppt</td>
</tr>
<tr>
<td>propene</td>
<td>-</td>
<td>30 ppt</td>
</tr>
<tr>
<td>n-hexane</td>
<td>-</td>
<td>5 ppt</td>
</tr>
<tr>
<td>benzene</td>
<td>-</td>
<td>26 ppt</td>
</tr>
<tr>
<td>toluene</td>
<td>-</td>
<td>40 ppt</td>
</tr>
</tbody>
</table>

$^1$ Initialization for June 2002; The background ozone in July is initialized as 38 ppb.

$^2$ The concentrations are initialized to keep the NO$_x$ background (PAN + HNO$_3$+NOX) as 460 ppt, the median summer concentrations of NO$_x$ at Jungfraujoch.

$^3$ Refer to Yienger et al. (1997).

7.3 Data analysis

7.3.1 Meteorological influence on diurnal variations of trace gas concentrations at Arosa

In Chapter 5, the frontal influence on ozone and its precursors at Arosa in the winter time has been discussed. The mean diurnal variations of days of the frontal type and fair weather type indicate the influence of meteorological conditions in summer (see Fig. 7-3). The influence of Foehn events are distinguished from these two weather types. The diurnal variation of foehn events are not considered because of the strongly variable timescale. Since the fronts do not arrive and depart exactly at the midnight, the days of the two weather types are selected by careful investigation and some days are excluded from the calculation of the diurnal variations of the two types.
As expected, NO$_y$ and ozone concentrations are much lower due to the wet deposition and titration by NO during frontal days than during fair weather days. The diurnal variation of ozone concentrations in summer has a maximum in the late afternoon at Arosa (Campana,
In dependent of the weather conditions, the ozone decrease in the morning is always found to be about 5 ppb. The morning air masses are from the nocturnal layer of the Arosa village, where strong ozone deposition and titration has taken place (Broder and Gygax, 1985).

The concentrations of CO, NOx and hydrocarbons under the different weather types are difficult to be explained. It appears that the morning air masses during frontal days are not as aged as during fair weather days: CO concentrations were lower and toluene concentrations were higher in the frontal types. The difference between toluene and CO is most possibly due to the change of solar radiation. About 50% CO originates from the photochemical production during oxidation of methane and non-methane VOCs (IPCC, 2001). Toluene was less degraded during the overcast days while the weaker photochemical production could lead to lower CO concentrations. The influence of weather conditions on the regional background is not obvious.

Since the background concentrations of the primary compounds are strongly dependent on the European contribution (see Section 7.3.2), the background concentrations of CO and hydrocarbons cannot be explained simply by the meteorological influence.

7.3.2 Concentrations of ozone and its precursors as a function of residence times in June and July 2002

The correlations between European residence times and trace gas concentrations in June and July 2002 are shown in Fig. 7-4, using a similar approach as described by Pochanart et al. (2001). In the comparison, we used only the measurements of early morning, which are least influenced by local emission. On days with suitable photochemical conditions (fair weather days, solid points in Fig. 7-4), excluding the special cases of background variation (1 and 2 in Fig. 7-6, see the discussion in Section 7.4.2), ozone concentrations have better correlations to the residence time than the correlations obtained considering all days during the two months (blank and solid points in Fig. 7-4).

CO and NOx concentrations also have some correlations to the residence times during fair weather days, though the correlations are worse than that for ozone. This is caused by the accumulation of primary pollutants from European emissions during the transport. The correlation for benzene is even worse than those for CO and NOx, because of the fast degradation during the transport. The contribution of the European emission for the reactive compounds at Arosa could have been balanced by the degradation during transport.
7. SIMULATIONS BY A CHEMICAL BOX MODEL

7.4 Results of the trajectory box model simulation

7.4.1 Sensitivities of ozone concentration to the initial concentrations and mixing process

The simulation of ozone concentration measured on the morning of 20 June at Arosa is chosen for sensitivity analysis. The initial values for the simulation are shown in Table 7-2. Figure 7-5 shows the simulated ozone increase along the averaged trajectory (of the ensemble of five) of 20 June 2002, assuming that the boundary layer height is 1300 m and the mixing takes place at 1500 CET every day, which is a virtual condition to estimate the efficient mixing time along the transport. The increase in ozone concentrations during the daytime is related to the emission strength of the grids involved along the transport. In the two days prior to 20 June, the air parcel moved through polluted areas in the north of Italy and the ozone concentration was strongly enhanced. The increase in ozone concentrations due to Italian emission is about 6 ppb/d. During foehn events in summer, the Po valley emission can lead to enhancement of ozone up to 5.6 ppb in summer (Campana et al., 2004). Therefore the simula-
 tion of the model could also be used to describe foehn events. In addition, the poor correlations between residence times and ozone concentrations during foehn events are also possibly related to the background variation beside the spatial distribution of emissions, for example, the air during some foehn events could be from the polluted Tripolis in North Africa.

The sensitivity analysis of the mixing hours per day and initial concentrations of ozone and CO is performed (see Fig. 7-5) under the following conditions: i) The mixing between the boundary layer and the residual layer happens for 2 hours, 1 hour and ½ hour per day. ii) Initial ozone concentrations are 42.6 ppb and 51.5 ppb, corresponding to 100% and 120% of the background from the trajectory approach; initial CO concentrations are 123 ppb and 148 ppb, corresponding to 100% and 120% of the mean CO concentrations in June at Jungfraujoch.

The simulated ozone concentration at Arosa is strongly dependent on the initial ozone concentration. The variation of background ozone concentrations leads to a large deviation, especially during the transport with a smaller residence time. However, the background variation of CO only leads to a small change of ozone concentration after a long range transport. The sensitivity to initial concentrations of individual hydrocarbons is also weak. If the background concentration of ethane is 10 times higher than the value in table 7-1, the ozone concentration will only increase by about 2% at the receptor site.

It is also found that the simulated ozone concentrations are strongly dependent on the input of European emission, determined by the mixing hours per day. One hour of mixing every afternoon during transport gives the best agreement with the measured ozone concentration at Arosa on the morning of 22 June (73 ppb).

![Fig. 7-5. Sensitivity analysis of ozone accumulation along trajectories. Left – for different initial concentrations, right – for different mixing times.](image)

### 7.4.2 Comparison between simulations and measurements of June and July 2002

Figure 7-6 shows that the agreement between simulated trace gas concentrations at Arosa, for early morning concentrations, is strongly dependent on the weather conditions. The days with the influence of fronts and foehn events are indicated by the horizontal lines below the
figure illustrating ozone concentrations. The agreement is quite satisfactory for ozone concentrations during fair weather days, while the disagreement is large in particular in the case of frontal disturbances, which were much more frequent in July than in June. During these conditions the concentrations of ozone and NO\textsubscript{y} are strongly overestimated. The overestimation of NO\textsubscript{y} and ozone concentrations for 11 to 16 July can be explained by the lack of wet deposition and titration in the numerical simulations.

**Fig. 7-6.** Simulation of ozone, CO and NO\textsubscript{y} concentrations for June-July 2002. The numbers show the special cases, in which large deviations of the simulation results are found, due to some errors discussed in Section 7.2.2.1.
7.4.3 Deficiencies in the chemical trajectory box model

In addition to difficulties of the simulations in case of fronts, there are other errors in the simple simulation, mainly attributed to the following two factors.

1) **Background variations.** In the assumption, the background is assumed to be uniform. However, some air masses from more polluted backgrounds can be identified. For example, the point marked by 2 in the Fig. 7-6 is from North Africa, probably includes the contribution of Tripolis. The ozone concentration in case 2 is much higher than that of the simulation. CO concentrations in the morning of the first two days in June, indicated by 1, are also much higher than those in the simulated values. Air masses in these two days were identified as coming from North America, when a consistent high pressure center dominated the North Atlantic. The intercontinental transport may possibly play an important role in this case. The westerly wind over the North Atlantic could lead to a transatlantic transport to Europe (Li et al., 2002). The enhanced CO concentrations also probably originated from the forest fire in Canada¹ at the end of May. As shown in the sensitivity analysis of ozone concentrations at Arosa, the influence of background ozone variation is dependent on the residence time. On the first two days in June, the residence time over Europe is very small, and we found obvious underestimation of ozone.

2) **Resolution of ECMWF data.** The coarse resolution of ECMWF trajectories can lead to some errors, especially over the complicated topography of the mountainous areas. If the air masses stay over the alpine region for a long time, the errors of ECMWF models could lead to higher deviations, for example the cases marked by 3, in which the air masses stayed over the alpine region for more than 2 days. The higher simulated concentrations of ozone and its precursors could be due to the underestimation of vertical dilution. However, it is not possible for this error to be detected in the simple model. The air masses which have stayed over the alpine region for more than 2 days are less reliable in the simulation by the simple model. In addition, the boundary layer heights at Jungfraujoch were not well predicted in ECMWF models over the complex mountainous terrain (De Wekker, 2002), where the errors were thought to be from the ECMWF boundary layer height routine.

Apart from some other factors, like the synoptic disturbance before the air arrives at Arosa, the use of EMEP emission with no consideration of the seasonal variation, as well as the lack of release of nighttime emission in the daytime mixing layer and the lack of other chemical mechanisms during the transport, can also lead to errors. However, these problems are not probably as important as the two mentioned above. The previous weather influence can even be compensated for by the following photochemistry in the transport.

The two simulation modules, the average of simulations upon five trajectories (Model II) and the simulation upon the average trajectory (Model I) sometimes have large differences (Fig. 7-6), though both have similar tendencies. To avoid the error from an individual trajectory, the results of Model II are considered as more reliable.

¹ http://cwfis.cfs.nrcan.gc.ca/en/current/cc_img_e.php
7.4.4 Correlations between simulated and measured concentrations of ozone and its precursors

The correlations between the simulation (from Model II) and the measurement are shown in Fig. 7-7, in which the problematic points caused by fronts, foehn events and the three cases discussed in Section 7.4.2 (shown by the blank points) were excluded from regression calculation. It is found that the cleanest air masses and the most polluted air masses are well simulated. However, the points were distributed over a large range from the 1:1 correspondence line, possibly caused by the variations in ozone background and the restricted resolution of ECMWF models.

![Graphs showing correlations between simulations and measurements of O3, CO, NOy, and toluene/benzene.](image)

**Fig. 7-7.** Correlations between simulations and measurements of (a) ozone, (b) CO, (c) NOy, and (d) toluene/benzene in June – July 2002. The solid points are from fair weather days and the blank points are from the days of fronts, foehn events and the special cases in Fig. 7-6. Correlation equations and coefficients are shown in the figure.

The ratios between hydrocarbon concentrations are also obtained from the simulation. Although the simulations of toluene/benzene ratios are much worse than the simulations of CO...
7. SIMULATIONS BY A CHEMICAL TRAJECTORY BOX MODEL

and NO\textsubscript{y} concentrations, the simulated toluene/benzene ratios are reasonable in comparison to the real values. They are scattered in a large range around 1. The lowest part is not found under realistic conditions, possibly because of the dilution in the alpine region.

The simulated ozone concentrations also have correlations to the residence times over Europe (not shown in the text). The correlation coefficients and slopes are quite similar to the results for the measurements.

However, it is found that the correlation of ozone concentrations to residence times (see Fig. 7-4 in Section 7.3) is better than the modeling results. This is not surprising since the dilution effect, which is not considered in the Lagrangian model, possibly leads to a spatially more uniform distribution in a considerably large area during the transport, especially when the air masses are influenced frequently by the mixing between the free troposphere and the boundary layer.

7.5 Conclusions

Ozone and NO\textsubscript{y} concentrations at Arosa during the summer frontal days are much lower than those under fair weather conditions. However, the influence of weather conditions on CO and hydrocarbon concentrations are not clear, which shows that the weather conditions have very weak influences on the vertical mixing strength in the Alpine region in summer.

The trajectory box model with EMEP emission and ECMWF boundary layer heights reproduces the transport process of the air masses over Europe under fair weather conditions. The simple trajectory box model can help to determine the contributions of European countries to ozone at Arosa. However, further limitations for example no consideration of the turbulent mixing during transport and poor resolution of the meteorological field are difficult to be resolved and may lead to some other uncertainties. The very simple method for the study on ozone concentrations at Arosa, using the trajectory approach (Pochanart et al., 2001), is comparable to the modeling results. The trajectory approach can be applied instead of the complicated chemical models to solve some particular problems as long as the gradients of the emissions over Europe and the variation in background ozone can be neglected under suitable weather conditions.
8 Comparison between simulations of two 3-D global models (GEOS-CHEM and MOZART) and measurements at Jungfraujoch

8.1 Introduction and concept of comparison

Several global and regional models have been developed to improve our understanding of the transport and transformation of primary pollutants and aerosols in recent years and to help on environmental assessment and policy making. Global models are valuable and widely used in the study of the global scale transport and budgets of trace species (Wild et al., 2001 and Li et al., 2002). With increasing knowledge of the atmospheric physics and chemistry, model development was fast in the last two decades. Present chemical transport models (CTMs) are developed based on the information of meteorological modules and provide the possibility for simulations of chemical species for specific time and receptor sites.

Global numerical simulations need simplifications, partially because of limited computer resources. However, the hemispheric tropospheric ozone cycle, which is also important with respect to radiative forcing, still includes large uncertainties (IPCC, 1996). Therefore, the comparison between the simulations and field measurements remains an important task for validating the reliability of the model results. The currently available evaluations of the models were mainly performed using the results of aircraft measurements and the measurements at coastal sites (e.g. Bey et al., 2001a; Horowitz et al., 2003). The comparisons between models have been carried out intensively from different perspectives and for different areas. Fiore et al. (2003) compared the simulations of ozone over the surface of the eastern United States and evaluated the influence of resolutions of GEOS-CHEM. An evaluation of several CTMs and GCMs with upper troposphere/lower stratosphere measurements of ozone and its precursors was recently presented by Brunner et al. (2003). Simulations for the mountain sites over the complex topography are not satisfactory because the mountain venting is difficult for the global models to resolve (Martin et al., 2003).

In this chapter, the outputs of two global models, GEOS-CHEM and MOZART are compared to the measurements of ozone and NO₃ from Jungfraujoch for 1993-1997 and the aspects of the global models in their description of ozone at remote sites are investigated. The measurement site Jungfraujoch is at an altitude of 3580 m asl, which is much higher than the surface altitude in the model. Because of the coarse resolution, global CTMs cannot resolve the complex transport processes in the Alps in any realistic way. However, as discussed in the preceding chapters, the background at Jungfraujoch is primarily the free troposphere, which can be simulated by the CTMs. In the comparison, the simulations at the real elevation of
Jungfraujoch are selected, which implies that the altitude is well above the planetary boundary layer in the model. The difference between the ozone simulations by GEOS-CHEM and MOZART is presented in Taylor diagrams, as used by Brunner et al. (2003).

8.2 Description of the dataset and methods

8.2.1 Dataset of measurements and simulations

The hourly average measurements of ozone and nitrogen oxides (NO\textsubscript{x}: NO + NO\textsubscript{2}) at Jungfraujoch in the period of 1993 to 1997 are obtained from the NABEL database. The comparison between the measurements and simulations is performed based on the point-by-point concentrations at 0000, 0600, 1200, 1800 UTC.

The MOZART simulations are from the latest version MOZART-2. The GEOS-CHEM simulations of 1993-1995 and 1996-1997 are from the earlier versions, GEOS-1 and GEOS-STRAT, individually. The only difference between GEOS-1 and GEOS-STRAT is the vertical resolution (see Table 8-1). The basic differences between GEOS-CHEM and MOZART are described in Table 8-1. It should be noted that in the simulation of GEOS-CHEM the winds are originally provided on 2° x 2.5° horizontal grids, but that results are shown for a simulation using winds regridded on 4° x 5° grids for computational expediency. The detailed descriptions of the GEOS-CHEM and MOZART models can be found in Bey et al. (2001a) and Horowitz et al. (2003).

<table>
<thead>
<tr>
<th>Table 8-1. Characteristics of the models, GEOS-1, GEOS-STRAT and MOZART-2</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Vertical levels</strong></td>
</tr>
<tr>
<td>20 levels (GEOS-1, 1985-1995)) to 10 hPa; 26 levels in a sigma coordination (GEOS-STRAT, 1996-1997) to 0.1 hPa</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th><strong>Horizontal resolutions</strong></th>
<th>2° lat ( \times ) 2.5° lon (see text)</th>
<th>1.9° lat ( \times ) 2° lon</th>
</tr>
</thead>
</table>

<table>
<thead>
<tr>
<th><strong>Layers below 650 hPa dynamical data</strong></th>
<th><strong>GEOS-CHEM</strong></th>
<th><strong>MOZART</strong></th>
</tr>
</thead>
<tbody>
<tr>
<td>Assimilated meteorological data from the Goddard Earth Observing System (GEOS) of the NASA data assimilation office (DAO)</td>
<td>Basic chemistry: Horowitz et al. (1998)</td>
<td>Assimilated meteorological fields from the European Centre for Medium Range Weather Forecast (ECMWF)</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th><strong>Chemistry</strong></th>
<th><strong>GEOS-CHEM</strong></th>
<th><strong>MOZART</strong></th>
</tr>
</thead>
</table>

<table>
<thead>
<tr>
<th><strong>Depositions</strong></th>
<th><strong>GEOS-CHEM</strong></th>
<th><strong>MOZART</strong></th>
</tr>
</thead>
<tbody>
<tr>
<td>Dry deposition: Wesely (1989) and Wang et al. (1998)</td>
<td>Dry deposition: Wesely (1989) and Hess et al. (2000)</td>
<td>Wet deposition: applied to the soluble species, including HNO\textsubscript{3}, H\textsubscript{2}O\textsubscript{2}, CH\textsubscript{3}O, organic hydroperoxides and Pb-210</td>
</tr>
<tr>
<td>Wet deposition: applied to HNO\textsubscript{3} and H\textsubscript{2}O\textsubscript{2}</td>
<td>Wet deposition: applied to HNO\textsubscript{3} and H\textsubscript{2}O\textsubscript{2}</td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th><strong>Emissions</strong></th>
<th><strong>GEOS-CHEM</strong></th>
<th><strong>MOZART</strong></th>
</tr>
</thead>
<tbody>
<tr>
<td>Emissions include the year-by-year variations Species considered: NO\textsubscript{x}, CO, isoprene, C\textsubscript{2}H\textsubscript{6}, C\textsubscript{3}H\textsubscript{8}, ( \geq )C\textsubscript{4} alkanes, ( \geq )C\textsubscript{3} alkenes and acetone</td>
<td>Emissions are representative for the early 1990s Species considered: NO\textsubscript{x}, CO, isoprene, C\textsubscript{2}H\textsubscript{6}, C\textsubscript{3}H\textsubscript{8}, C\textsubscript{2}H\textsubscript{4}, C\textsubscript{3}H\textsubscript{6}, C\textsubscript{4}H\textsubscript{10}, acetone, C\textsubscript{10}H\textsubscript{16}, CH\textsubscript{2}O, CH\textsubscript{3}OH, CH\textsubscript{4}, N\textsubscript{2}O and H\textsubscript{2}</td>
<td></td>
</tr>
</tbody>
</table>
The on-the-spot pressure at Jungfraujoch is about 640-670 hPa. Several closest vertical levels in MOZART and GEOS-CHEM are considered in the comparison. The altitudes of these levels are given in Table 8-2. The output of the 7th level (606-682 hPa – GEOS-1; 627-697 hPa – GEOS-STRAT) in GEOS-CHEM and the 8th level (658-696 hPa) in MOZART are used to make the comparison, considering that a level slightly lower than the “real” altitude could catch the flow influenced by the surface, in consideration of the topography of the alpine region.

Table 8-2. Vertical levels in GEOS-CHEM (G) and MOZART (M).

<table>
<thead>
<tr>
<th>Middle pressure (hPa)</th>
<th>Boundary pressure (hPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>M5 788</td>
<td>771-805</td>
</tr>
<tr>
<td>M6 753</td>
<td>735-771</td>
</tr>
<tr>
<td>M7 715</td>
<td>696-735</td>
</tr>
<tr>
<td>M8 677</td>
<td>658-696</td>
</tr>
<tr>
<td>M9 638</td>
<td>619-658</td>
</tr>
<tr>
<td>M10 599</td>
<td>580-619</td>
</tr>
<tr>
<td>G5 790; 796*</td>
<td>756-824; 765-828</td>
</tr>
<tr>
<td>G6 719; 731</td>
<td>682-756; 697-765</td>
</tr>
<tr>
<td>G7 644; 663</td>
<td>606-682; 628-697</td>
</tr>
<tr>
<td>G8 568; 595</td>
<td>530-606; 561-628</td>
</tr>
</tbody>
</table>

* GEOS vertical level: GEOS-1; GEOS-STRAT

8.2.2 Taylor diagrams

The correlation coefficient \( R \) is not sufficient to quantify the similarity between two series (a model field \( f \) and a reference field \( r \)), because the amplitude difference between two patterns is not described by the correlation coefficient. The most commonly used statistical quantity for quantifying differences in two fields is the root mean square (RMS) difference \( (E') \). The correlation coefficient and RMS difference are defined respectively as:

\[
R = \frac{1}{\sigma_f \sigma_r} \sum_{n=1}^{N} (f_n - \bar{f})(r_n - \bar{r}), \quad \text{(8-1)}
\]

\[
E' = \left\{ \frac{1}{N} \sum_{n=1}^{N} \left[ (f_n - \bar{f}) - (r_n - \bar{r}) \right]^2 \right\}^{\frac{1}{2}}, \quad \text{(8-2)}
\]

Taylor (2001) suggests describing the correlation coefficient and the RMS difference, as well as the standard deviations of the model field \( \sigma_f \) and the reference field \( \sigma_r \) in a two-dimensional statistical diagram. There is a relationship between the four statistical quantities:

\[
E'^2 = \sigma_f^2 + \sigma_r^2 - 2\sigma_f \sigma_r R \quad \text{(8-3)}
\]
which is represented in Taylor diagrams based on the law of cosines, as described in Taylor (2001). In Taylor diagrams, the RMS difference is the distance between the model and reference point.

Besides the three parameters which are included in Taylor diagram, the absolute difference between the model and reference values is also important. The overall bias, the mean difference of the model field from the reference field, is also considered in the comparison.

8.3 Seasonal variations of ozone concentrations

The seasonal variations of ozone from simulations are calculated based on the concentrations at the selected points and the outputs are not considered when there is no ozone measurement at Jungfraujoch.

The model outputs of M8 and G7 are compared in Fig. 8-1 and 8-2. Figure 8-1 shows the seasonal mean ozone concentrations of the model outputs and measurements. Both models reproduce qualitatively the seasonal variation of ozone concentrations at Jungfraujoch, but overestimate ozone concentrations in winter, in particular in the period of 1993-1995.

![Fig. 8-1. Monthly mean ozone concentrations at Jungfraujoch and the mean ozone concentrations simulated by MOZART and GEOS-CHEM. The error bars indicate the standard deviations. The grey line shows the ozone concentrations without the “local” boundary layer influence, filtered by NOx measured/NOx simulated ≤ 4.](image)

![Fig. 8-2. Monthly median NOx concentrations at Jungfraujoch simulated by MOZART and GEOS-CHEM (left axis) and monthly median measured NOx concentrations (right axis). The measurements in September to December 1995 and May 1996 are not available.](image)
8. COMPARISON BETWEEN GEOS-CHEM AND MOZART

The observed NO\textsubscript{x} concentrations are much higher than the simulated values, suggesting that the alpine venting in convective weather conditions as well as front and foehn disturbances are hardly captured in the models (see Fig. 8-2). The monthly median NO\textsubscript{x} concentrations from the two models are quite similar and the lowest median concentrations are found in winter seasons because of the weaker vertical mixing in winter.

In addition, we tried to remove such episodes when strongly polluted air masses from the planetary boundary layer (e.g. fronts and foehn events) were monitored at Jungfraujoch by a NO\textsubscript{x} filter. When NO\textsubscript{x} measurements exceeded the simulation by more than a factor of 4, the points were excluded. After excluding the boundary layer influence, better correlations can be obtained for the simulations, though the improvements are very small.

The filtered monthly mean ozone concentrations are also found not to be much different from original concentrations (see the grey line in Fig. 8-1). The filtered mean concentration in 1993-1997 without the boundary layer influence is only about 1 ppb higher than that of the entire dataset. It suggests that the local or synoptic lifting (front and foehn events) does not contribute very much to the monthly mean ozone concentrations in reality. The improvements of the correlations between simulations and observations by using the filter are also very small for both models (not included in this chapter). In the investigation on the inversion days in November and December by Campana (2003), the ozone mean concentration during days when temperature inversions over the Swiss plateau were observed is found to be about 2 ppb higher than the mean of the two months, which is close to the result in Fig. 8-1.

8.4 Time series

Figure 8-3 gives an example of the comparison between simulations and measurements, based on the simultaneous data every 6 hours. The three lines clearly have similar tendencies of ozone variation. However, the ozone variation described by GEOS-CHEM is systematically smaller than that of the measurements or the output of MOZART. Most of time, concentrations of NO\textsubscript{x} are lower than 0.1 ppb for both the measurements and simulations. The enhancements of NO\textsubscript{x} in observations are not well described in both models.

8.5 Comparison in Taylor diagrams

In the following subsections, the two fields from the point-by-point output of ozone concentrations from GEOS-CHEM and MOZART are compared to the measured ozone concentrations (reference field) in Taylor diagrams, in which the points are normalized by the observation field.
8. COMPARISON BETWEEN GEOS-CHEM AND MOZART

8.5.1 Comparison upon different levels

The five-year overall measurement dataset is compared to the simulations in Fig. 8-4. The correlation coefficients for the two models are quite similar in a small range of 0.50-0.63. The outputs of the lower level (M5 and G5) have higher correlation coefficients and standard deviations probably because the lower levels captured the influence of surface emissions. However, the overall biases are found to be smallest in the model outputs of M7 and G6 (Fig. 8-6). The overall bias of MOZART is higher than that of GEOS-CHEM. It is also found that the bias of the MOZART simulation becomes positive when the altitude is lower than M7, in contrast to that of GEOS-CHEM.

Fig. 8-4. Taylor diagram for the comparison of ozone measurements at Jungfraujoch with the outputs of the global models GEOS-CHEM (green) and MOZART (blue) for data from different vertical levels for five years. Their altitudes are listed in Table 8-2.
8.5.2 Comparisons by different seasons (winter and summer)

When separated into different seasons (winter and summer, see Fig. 8-5), correlations become worse for both models, obviously because both models are missing the contribution of seasonal variation. The overall biases (Fig. 8-6) in different seasons suggest that the magnitudes of biases are determined by the winter seasons, when both models overestimate the ozone concentrations. The trend of biases upon different altitudes is determined by the summer season. M8 and G7 give smallest biases in summer. The overestimated ozone concentrations of both models during the winter season might be related to the underestimation of the influence of surface emissions, leading to ozone titration by NO.

The winter time correlation coefficients for MOZART are better than those in summer, especially for the simulations of the levels higher than M7-M9 while the GEOS-CHEM performance is worse in winter. Since the wintertime ozone concentrations are determined primarily by the transport, the MOZART model probably has better capability to describe the long range transport.

Fig. 8-5. Taylor diagram of the comparison of ozone measurements at Jungfraujoch with the output of the global models GEOS-CHEM (G) and MOZART (M) for four summers (June-August) 1993, 1994, 1995 and 1996 for output of different levels (orange) and data for four winters (December-February), 1993-1994, 1994-1995, 1995-1996 and 1996-1997 (blue).

Fig. 8-6. Overall biases of the simulation at different levels. Bars in orange, blue and white are representative for summer, winter and all data, respectively. The statistical comparison for summer and winter are described in Fig. 8-5.
8. COMPARISON BETWEEN CEOS-CHEM AND MOZART

8.5.3 Comparison by different years

A year-by-year investigation (Fig. 8-7) shows that the correlation coefficients for GEOS-CHEM simulations are slightly higher than those for MOZART (except 1997) while the simulations of MOZART have standard deviations closer to the observations. The differences between ensembles of the simulations of GEOS-CHEM and MOZART over the five years indicate the characteristic differences between the two models. However, the RMS differences for the two models are similar, suggesting comparable performances of the two CTMs. In the point-by-point comparison of several global models by Brunner et al. (2003), the correlation coefficients of the correlations between the simulations by five CTMs and two GCMs and measurements in the upper troposphere over the North Atlantic region were about 0.5-0.75. In reproducing the exchange between troposphere and stratosphere, the standard deviations of some models were even higher than the measurement results, but the large deviations were not related to the spatial resolutions (Brunner et al. 2003). The simulations of ozone concentrations at Jungfraujoch from GEOS-CHEM and MOZART have correlation coefficients of 0.4-0.7, close to the results of the evaluation of several CTMs by aircraft measurements over the North Atlantic region by Brunner et al. (2003).

![Fig. 8-7. Taylor diagram for the GEOS-CHEM (circles) and MOZART (crosses) simulations in individual years. The points of different colors (blue, pink, light blue, yellow and brown) represent the results from 1993 to 1997](image)

8.6 Conclusions

The surface altitudes of the two global CTMs, GEOS-CHEM and MOZART are much lower than the on-the-spot altitude of Jungfraujoch measurement stations, which is at the height of vertical levels, M8 and G7, (see Table 8-2). The simulations upon these two levels reproduce the seasonal variation of ozone concentrations at Jungfraujoch. However, neither of the models reproduces the boundary layer influence which is found intermittently at the altitude of Jungfraujoch. This contribution identified using a filter on the NOx data appears to have only a small influence on ozone concentration at Jungfraujoch. It decreases the ozone
concentration at Jungfraujoch by about 1 ppb in 1993-1997. Although the alpine venting was thought to contribute to the free tropospheric ozone (Henne et al., 2003), the contribution to ozone at Jungfraujoch is probably small.

In the statistical analysis, three parameters (the correlation coefficient, standard deviation and overall bias) are considered. The comparison shows the difficulties of the comparison between models and measurements over the continental surface. As found in the time series (Fig. 8-2), the simulations by MOZART have comparable standard deviations to the measurements while the standard deviations of GEOS-CHEM are much lower than the observations. This might be partially caused by the different horizontal resolutions. The simulations by GEOS-CHEM and MOZART have similar correlations with the observations and the tendencies upon vertical levels are also similar. The best correlation coefficients are found upon lower levels, in which the influences of surface emission on a local or regional scale are possibly captured to some extent. After separating the results for winter and summer, it is found that the outputs of both models have higher biases in winter, while smaller absolute biases are found in summer. The summer data can be simulated with smallest absolute overall biases upon the level (M8 and G7) of on-the-spot altitude of Jungfraujoch. For the winter time simulation, lower levels are more satisfactory, in consideration of the overall biases. A higher correlation coefficient is found in winter than in summer for the MOZART model (Fig. 8-6), suggesting that the long range transport is well reproduced by MOZART. However, because the ozone variations in winter is smaller than in summer, the lower resolution of the wind field in GEOS-CHEM could be the reason of worse correlations in winter. Despite all the differences mentioned above, the close RMS errors for the yearly dataset and the overall dataset show that the performances of two models are not that different.

Since the two models were developed independently by two research teams, many differences exist between them. The differences in correlation coefficients and standard deviations are possibly determined by the meteorological fields, especially the model resolutions, but their relationship is not clear (Brunner et al., 2003).
9. Summary and Conclusions

Measurements of volatile hydrocarbons and NO$_x$, NO$_y$ and ozone (as part of the thesis of Campana) were performed at the alpine site Arosa for more than one year in order to study the meteorological influences on the transport and transformation of the trace gases. The complete dataset of trace gas measurements at Jungfraujoch and Arosa provides further information on the influences of the alpine air flow and synoptic weather conditions on the trace gas concentrations. The seasonal variations of median hydrocarbon concentrations at both sites are quite similar. However, the concentrations of hydrocarbons at Jungfraujoch are smaller than those at Arosa because Jungfraujoch is more exposed to the free troposphere than Arosa.

The diurnal variations of hydrocarbons reflect the exchange between the alpine boundary layer, the injection layer and the free troposphere. The up-slope wind transports the emissions of closest valleys to Arosa in the morning and to Jungfraujoch in the late afternoon. The contributions of the closest valley emissions are compared to the ratios of the hydrocarbon concentrations in Zürich and it is found that the hydrocarbons at Arosa are mainly from the traffic emission. Other sources, however, like solvent usage and gasoline evaporation, are also important in the closest valleys around Jungfraujoch. The so-called contributions of the closest valleys at Jungfraujoch could be far away from Jungfraujoch. These emissions are possibly injected into the free troposphere in the upwind direction of Jungfraujoch.

The meteorological influences on trace gas concentrations at Jungfraujoch and Arosa are investigated in Chapter 5. The meteorological variation results in complicated patterns of the concentrations of the trace gases. A coarse discrimination between the frontal disturbance and the thermal circulation disturbance is suggested in the perspective of transport scales: local thermal circulation, synoptic lifting and free tropospheric transport. The European boundary layer influence at Jungfraujoch has two patterns: up-valley venting with smaller amounts of pollutants, and synoptic lifting with large amounts of pollutants. Furthermore, free tropospheric air masses in winter are studied at both sites. It was believed that the Jungfraujoch stays in the free troposphere most of time during convective days in winter (Schuepbach et al., 2001), when there is a persistent temperature inversion over Swiss plateau. However, the dilutions in the alpine region cannot be completely blocked by the temperature inversion. The comparison of trace gas concentrations at Arosa and Jungfraujoch in winter suggests that Arosa was frequently influenced by the “leak” over the alpine region by the thermal lifting, which can transport primary pollutants from the Swiss Plateau to the high alpine sites above the inversion layer. Free tropospheric air at Jungfraujoch is detected by the toluene/benzene ratios. Several cases are found from intercontinental transports in the cold season, docu-
mented by backward trajectories. The concentration of OH radicals in the path of the intercontinental transport is estimated to be $5.1 \times 10^5$ cm$^{-3}$.

In contrast to Jungfraujoch, Arosa is in the alpine boundary layer in the daytime, in which the air is normally more polluted. During the convective days, there are different backgrounds at the two places. Only in synoptic events are the backgrounds comparable at both sites (see Section 5.2). Because of the influence of the alpine injection layer, it is even more difficult to get a source-receptor relation by trajectories at the mountain sites, like Arosa. The statistical trajectory approach in Pochanart et al. (2001) is a suitable and simple-to-use tool to study ozone and its precursors at Arosa. However, the application is limited by the weather conditions. In winter, the decrease in ozone concentrations happens when the air masses are transported in the boundary layer and a tendency for ozone concentrations to increase is found during the fair weather days, when temperature inversions exist over the Swiss Plateau. The ozone accumulation in winter is determined by the photochemistry of the ozone precursors from the “leaks” of temperature inversions. In addition, it is noticed that the fast frontal passage at Arosa in winter and spring could lead to an underestimation of background ozone concentrations when the trajectory approach proposed by Pochanart et al. (2001) is used without considering the weather influence.

ECMWF and aLMo trajectories are compared statistically based on the lifting cases in Chapter 6. The largest difference exists under the weather type of northerly advection. The forecast aLMo trajectories are found to be no more accurate than the reanalysis ECMWF trajectories, in spite of the better resolutions. However, the dependence of the forecast aLMo trajectories on weather conditions helps to distinguish the frontal passage from other weather types. The result of the comparison supports the applicability of aLMo trajectories for synoptic lifting at Jungfraujoch, as suggested by Zellweger et al. (2002). Generally, ECMWF trajectories of different receptor heights have different paths. The lower ECMWF trajectories are more available for describing the boundary layer influence.

In Chapter 7, a chemical trajectory box model is further developed to describe the transport of trace gas concentrations to Arosa, assuming a uniform background over the Atlantic Ocean. The ECMWF trajectories and EMEP emissions are integrated into the model. The simulation gives reasonable results compared to the measurements at the receptor site Arosa. The deviations of the simulated concentrations of ozone, CO and NOy concentrations from the real concentrations are mainly caused by the background variations and the dilutions over alpine regions, which are not possible to solve by the simple Lagrangian models. The simulation during these meteorological conditions is not considered because ECMWF trajectories could be less accurate, and the chemistry during the frontal passage is more complicated with the involvement of cloud and heterogeneous chemistry. The simulation during thunderstorms is still a challenging work for the regional and global models. The result of the simulation gives reasonable support to the trajectory statistical analysis of Pochanart et al. (2001). However, some comments are given to the trajectory approach in Pochanart et al. (2001). Because of the influence of the meteorology and background variations, the estimate of hemispheric background and European boundary layer influence is unreliable, especially in winter, although the concept of ozone accumulation is reasonable. The trajectory approach is probably too coarse to estimate the hemispheric background in reality, and the enhancement of
background concentrations caused by the intercontinental transport makes the definition of hemispheric background problematic. The global CTMs would be the better choice for the study of variations in the large scale transport.

Global models are suitable tools for the studies of the transport and transformation of species on a continental or global scale. Normally the air masses found at the receptor sites in a remote mountainous region have the contributions of various sources, which could only be identified by the global models. In Chapter 8, we compared two well-known global Chemical Transport Models, GEOS-CHEM and MOZART with ozone measurements at Jungfraujoch to learn about the performance of global models at a mountain site. The ozone seasonal variation at Jungfraujoch was well reproduced by the two models. In both global models, a description of the alpine venting is not included and even the frontal lifting is not well reproduced because of the resolution. However, the venting and synoptic lifting contribution to ozone concentrations at Jungfraujoch is very small, since the ozone concentration only decreases 1 ppb after using the NOx filter (measurements/modeling > 4) to remove the polluted cases.

Three methods, a trajectory statistical analysis, a Lagrangian photochemical box model and 3D CTMs are considered in the thesis. To some extent, all of them are applicable to the research on source-receptor relationships at a mountainous area. However, large uncertainties caused by the complex topography exist, which cannot be solved by the current meteorological models.
## Acronyms and abbreviations

<table>
<thead>
<tr>
<th>Acronym</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>aLMo</td>
<td>Alpine Model</td>
</tr>
<tr>
<td>asl.</td>
<td>above sea level</td>
</tr>
<tr>
<td>AWS</td>
<td>Alpine Weather Statistics</td>
</tr>
<tr>
<td>CET</td>
<td>Central Europe Time</td>
</tr>
<tr>
<td>CTMs</td>
<td>Chemical Transport Models</td>
</tr>
<tr>
<td>DWD</td>
<td>Deutscher Wetterdienst</td>
</tr>
<tr>
<td>ECMWF</td>
<td>European Center for Medium Weather Forecast</td>
</tr>
<tr>
<td>EMEP programme</td>
<td>Co-operative Programme for Monitoring and Evaluation of the Long-Range Transmission of Air pollutants in Europe</td>
</tr>
<tr>
<td>GAW</td>
<td>Global Atmosphere Watch</td>
</tr>
<tr>
<td>GC-FID (MS)</td>
<td>Gas Chromatography – Flame Ionization Detection (Mass Spectrometry)</td>
</tr>
<tr>
<td>GC-Ms</td>
<td>General Circulation Models</td>
</tr>
<tr>
<td>IPCC</td>
<td>Intergovernmental Panel on Climate Change</td>
</tr>
<tr>
<td>LPDM</td>
<td>Lagrangian Particle Dispersion Model</td>
</tr>
<tr>
<td>MCM</td>
<td>Master Chemical Mechanism</td>
</tr>
<tr>
<td>NABEL</td>
<td>the Swiss air pollution monitoring network (German)</td>
</tr>
<tr>
<td>NCEP</td>
<td>National Centers for Environmental Prediction</td>
</tr>
<tr>
<td>NGM</td>
<td>Nested Grid Model</td>
</tr>
<tr>
<td>NPL</td>
<td>National Physical Laboratory</td>
</tr>
<tr>
<td>TSP</td>
<td>total suspended particulate matters</td>
</tr>
<tr>
<td>VOTALP</td>
<td>Vertical Ozone Transport in the Alps</td>
</tr>
<tr>
<td>UTC</td>
<td>Universal Time</td>
</tr>
</tbody>
</table>
Appendix A:

A1. Special events in December 2001

It was found that the median concentrations of pentanes are higher at Jungfraujoch than at Arosa in December. This is caused by two special cases at Jungfraujoch, as the shaded periods show in Fig. App-1. The first case happened under anti-cyclonic conditions, with downward transport of air masses. The highest concentrations of primary pollutants, including CO, benzene and iso-pentane occurred during the nighttime and they were even higher than the concentrations at Arosa. Trajectories show that the air masses are most likely to be from an intercontinental transport. Two of these air masses (every six hours) have obvious transatlantic transport paths (See Table 5-2 in Section 5.4). The very low NO$_2$ concentrations at Jungfraujoch also suggest that the air masses did not originate from a local or regional source.

The second case occurred after the passage of a cold front. This time, a stratospheric intrusion with strong turbulence was found by the backward trajectories. However, the enhanced concentrations of primary pollutants indicated that the boundary layer air was enveloped into the stratospheric air. Also in this case, ozone concentrations were not extremely high because of the intensive mixing that took place before the air masses reached Jungfraujoch.

![Fig. App-1. The meteorological information at Arosa and Jungfraujoch.](image-url)
Fig. App-2. Comparison between concentrations of ozone and its precursors at Jungfraujoch (grey) and Arosa (black) in December 2001 (black).
The striking thing is that the extremely high iso-pentane concentrations are found in both cases. The high concentrations of iso-pentane have the characteristics of urban sources, as the concentration ratio between iso-pentane and benzene is even higher than 2.

**A2. Ratios between iso-pentane/n-pentane**

In contrast to the ratios of toluene/benzene, the iso-pentane/n-pentane ratios are not determined by the oxidation state. They are rather determined by the emission profiles. Staehelein et al. (1997) gave a statistical analysis on the different sources. The ratio is about 2 in the on-road traffic, while it is about 1 in the gasoline evaporation. The ratio of iso-pentane/n-pentane in the European boundary layer is higher than that in the marine boundary layer, because there is no gasoline evaporation over the sea (Wayne, 2003). The characteristic ratio of iso-pentane/n-pentane in the Arctic marine boundary layer is about 0.5 (Hopkins et al., 2001), which is determined by the oceanic biogenic emission (Broadgate et al., 1997). Although the iso-pentane/n-pentane ratios at Arosa, Jungfraujoch and Zürich do not differ in their distribution patterns as much as the ratios of toluene/benzene, their distributions still show a tendency similar to the toluene/benzene ratios: the smallest values (<1) are found mostly at Jungfraujoch and the distribution at Arosa is more compact.

The air masses with lowest toluene/benzene and iso-pentane/n-pentane ratios are investigated using 10 days backward ECMWF trajectories starting at 670 hPa. The backward trajectories showed that air masses of lowest iso-pentane/pentane ratios normally originate from the marine boundary layer either over the Arctic Ocean or over the Atlantic Ocean. Case (a) in Fig 5-8, Section 5.3.3 is an example with lower concentration ratios of iso-pentane to n-pentane. The trajectory ensemble normally has a large spatial scattering in the transports from the marine boundary layer. These events are not further investigated because of the complex transport processes of these air masses.

**Fig. App-3.** Distribution fractions of iso-pentane/n-pentane in Zürich, Arosa and Jungfraujoch. Data are from July 2001 to August 2002

Indeed there is no clear definition on hemispheric background. Normally the hemispheric background is thought not to be influenced by regional and local emissions. At the alpine
mountain sites, the hemispheric background concentrations are thought of as air masses over Atlantic Ocean (Pochanart et al., 2001). This hemispheric background could include both the air masses from the long range intercontinental transport and the air masses from the marine boundary layer. The smaller minimum of iso-pentane/n-pentane at Jungfraujoch also shows that the air masses at Jungfraujoch have a smaller contribution of European emissions.

A3. Seasonal variations of hydrocarbon concentrations in Zürich

The hydrocarbon concentrations in an urban area are mainly determined by emission intensity. The meteorological conditions like stability of the boundary layer also have some influence on the hydrocarbon concentrations. The seasonal variations of hydrocarbon concentrations in the remote sites are discussed in Chapter 4. The emission variations in an urban area are also shown in this appendix to get some understanding on the variation of urban emissions. The most important sources for hydrocarbons considered in this thesis are traffic emission, gasoline evaporation and solvent usage. The primary hydrocarbon source, traffic emission is assumed not to depend on the seasons while gasoline evaporation, which is important for the emission of pentanes, has strongly dependence on the ambient temperature. Solvent usage, an important emission sector for toluene and higher aromatic hydrocarbons is mainly related to the control of operation process, which is also less directly related to the seasons.

Figure App-4 shows the monthly median concentrations of several hydrocarbons in Zürich from July 2001 to June 2002. Iso-pentane and n-pentane have higher concentrations in summer, because of the stronger gasoline evaporation. Benzene and butanes have higher concentrations in winter, which is probably caused by the temperature inversion as well as the longer lifetime of these compounds in winter. For toluene and o-xylene, higher concentrations are found in the fall 2001. The seasonal variations of the hydrocarbons clearly show the variations of the different emission sectors in the urban area.
Fig. App-4. Monthly median hydrocarbon concentrations together with the 25 and 75 percentiles in Zürich.
### Appendix B:

Table App-1. The frontal events at Jungfraujoch together with other boundary layer disturbances. Fronts are detected by daytime relative humidity (>80%) and the Berlin weather charts.

<table>
<thead>
<tr>
<th>Frontal lifting events</th>
<th>Fronts (c-cold and w-weak)</th>
<th>AWS weather type</th>
<th>Others</th>
</tr>
</thead>
<tbody>
<tr>
<td>01.09.01</td>
<td>C</td>
<td>4</td>
<td>8, 10-12 September: high RH, persistent of frontal passage</td>
</tr>
<tr>
<td>04.09.01</td>
<td>C</td>
<td>3</td>
<td>18-19 September: south foehn, not caused by fronts</td>
</tr>
<tr>
<td>05.09.01</td>
<td>W</td>
<td>4</td>
<td>17, 20-21 September: high RH, persistent of frontal passage</td>
</tr>
<tr>
<td>07.09.01</td>
<td>C</td>
<td>4</td>
<td>29-30 September: south foehn at midnight, not caused by fronts</td>
</tr>
<tr>
<td>09.09.01</td>
<td>C</td>
<td>3</td>
<td></td>
</tr>
<tr>
<td>14.09.01</td>
<td>C</td>
<td>2</td>
<td>8, 10-12 September: high RH, persistent of frontal passage</td>
</tr>
<tr>
<td>16.09.01</td>
<td>C</td>
<td>3</td>
<td>18-19 September: south foehn, not caused by fronts</td>
</tr>
<tr>
<td>23.09.01</td>
<td>W</td>
<td>5</td>
<td></td>
</tr>
<tr>
<td>24.09.01</td>
<td>W</td>
<td>5</td>
<td>20 October: south foehn, caused by cold fronts</td>
</tr>
<tr>
<td>25.09.01</td>
<td>W</td>
<td>6</td>
<td>25 October: high RH, persistent of frontal passage</td>
</tr>
<tr>
<td>30.09.01</td>
<td>C</td>
<td>6</td>
<td>31 October: fast passage of cold front at night</td>
</tr>
<tr>
<td>08.10.01</td>
<td>C</td>
<td>8</td>
<td>1 October: fast passage of warm front at midday</td>
</tr>
<tr>
<td>09.10.01</td>
<td>C</td>
<td>8</td>
<td>3 October: fast passage of cold front at night</td>
</tr>
<tr>
<td>20.10.01</td>
<td>C</td>
<td>2</td>
<td>6-7 October: midnight south foehn, not caused by fronts</td>
</tr>
<tr>
<td>21.10.01</td>
<td>W</td>
<td>6</td>
<td>20 October: south foehn, caused by cold fronts</td>
</tr>
<tr>
<td>24.10.01</td>
<td>W</td>
<td>6</td>
<td>25 October: high RH, persistent of frontal passage</td>
</tr>
<tr>
<td>07.11.01</td>
<td>W</td>
<td>8</td>
<td>10-12 November: high RH, persistent of frontal passage</td>
</tr>
<tr>
<td>08.11.01</td>
<td>C</td>
<td>3</td>
<td>14 November: high RH, persistent of frontal passage</td>
</tr>
<tr>
<td>09.11.01</td>
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<td>4</td>
<td>24-26 November: high RH, persistent of frontal passage</td>
</tr>
<tr>
<td>13.11.01</td>
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</tr>
<tr>
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<td>8</td>
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</tr>
<tr>
<td>27.11.01</td>
<td>C</td>
<td>6</td>
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</tr>
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<td>28.11.01</td>
<td>C</td>
<td>6</td>
<td></td>
</tr>
<tr>
<td>29.11.01</td>
<td>W</td>
<td>6</td>
<td></td>
</tr>
<tr>
<td>30.11.01</td>
<td>W</td>
<td>4</td>
<td></td>
</tr>
<tr>
<td>05.12.01</td>
<td>C</td>
<td>8</td>
<td>1-4 December: high RH, warm front</td>
</tr>
<tr>
<td>06.12.01</td>
<td>C</td>
<td>4</td>
<td>6 December: cold front lasted until midday</td>
</tr>
<tr>
<td>11.12.01</td>
<td>C</td>
<td>4</td>
<td>14 December: high RH, persistent of frontal passage</td>
</tr>
<tr>
<td>13.12.01</td>
<td>C</td>
<td>4</td>
<td>25 December: high RH, persistent of frontal passage</td>
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<td>20.12.01</td>
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<td>29 December: high RH, persistent of frontal passage</td>
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</tr>
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<td></td>
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<td>30.12.01</td>
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</tr>
<tr>
<td>24.01.02</td>
<td>W</td>
<td>3</td>
<td>20, 28 January: very fast frontal passage</td>
</tr>
<tr>
<td>06.02.02</td>
<td>C</td>
<td>6</td>
<td>31, January – 1 February, midnight, fast passage of a cold front</td>
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</tr>
<tr>
<td>08.02.02</td>
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<td>4</td>
<td>20, 22, 26, 27 February: RH high, the persistent of frontal influence</td>
</tr>
<tr>
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</tr>
<tr>
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</tr>
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<td>15.02.02</td>
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</tr>
<tr>
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<td>Weather</td>
<td>AWS Type</td>
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<td>-----------</td>
<td>---------</td>
<td>----------</td>
<td></td>
</tr>
<tr>
<td>16.02.02</td>
<td>W</td>
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<td>18.02.02</td>
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<td>19.02.02</td>
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**Notes:**
- 2 March: south foehn, persistent of front passage
- 9 March: very fast passage of cold front
- 14 March: south foehn
- 20 March: high RH, the persistent of front passage
- 3-4 April: south foehn, midnight
- 10-11 April: south foehn, caused by weak fronts
- 18, 20 April: high RH, persistent of front passage
- 1-2 May: south foehn, caused by weak fronts
- 8 May: south foehn
- 19 May: RH high, the persistent of front passage
- 13 May: south foehn
- 22-23 May: south foehn
- 25-29 May: high RH, a low situated over alpine region; AWS weather types of these days are 6 6 5 5 6
- 5 Jun: south foehn, caused by cold front
- 19-20 June: south foehn
- 4 July: warm front followed by sharp downward transport
- 5-July: foehn caused by weak fronts
- 26 July: high RH, persistent of front passage
### APPENDIX B

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¹ Frontal passage together with foehn events  
² Cold fronts from the south direction
Appendix C:

It is also possible to use the height over ground (HOG) to show the influence of boundary layer at Jungfraujoch, especially as the air masses from the alpine boundary layer carried fresh emission. Contrary to the altitudes of trajectories, HOGs are more suitable for the identification of the air masses from the closest valleys, which are at a high altitude above sea level. The possibility of trajectories to show the lifting cases most of all in the indifferent convective days are determined by this parameter.

The HOGs (hPa) are included in the aLMo trajectories. The HOGs for ECMWF trajectories are calculated by the difference between the backward pressure and surface pressure over the grid points. The correlations between the HOGs calculated in the previous 24 hours and the concentrations of primary pollutants at Jungfraujoch are shown in Table App-2. The correlations are determined by the difference between boundary layer and free troposphere. In both seasons, the best correlations for both trajectories are found for toluene and ln(toluene/benzene). Correlations for ECMWF trajectories are better than aLMo trajectories, as mentioned in Chapter 6.

Table App-2. Correlation coefficients (r) between trace gas concentrations and the HOG (hPa) in the previous 24 hours before arriving at Jungfraujoch. Each correlation contains at least 300 points. The correlation coefficients higher than 0.25 are highlighted. 650,…,810 – 650 hPa, …, 810 hPa ECMWF trajectories; lm700 and lm100 – aLMo trajectories with starting point at 700 hPa and 100 m over ground. w – winter; s – summer.

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