Reactive Nitrogen (NO$_y$) at the High-Alpine Site Jungfraujoch

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

Presented by

Christoph Zellweger
Dipl. Chem. ETH
born December 19, 1964
citizen of Teufen (AR)

accepted on the recommendation of
Prof. Dr. Renato Zenobi, examiner
PD Dr. Urs Baltensperger, co-examiner
Dr. Peter Hofer, co-examiner

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Summary

Nitrogen compounds play a central role in the chemistry of the atmosphere. They are involved in the formation of acid precipitation as well as of tropospheric ozone. Despite their importance there are still relatively few studies available of the distribution of the major nitrogen compounds in the atmosphere. In particular, only few measurements of the remote troposphere over Europe have been published.

In this work, measurements of the sum of all reactive nitrogen compounds (NO$_y$) were conducted over a two-year period at the high-alpine research station Jungfraujoch (JFJ). Total NO$_y$ is defined as the sum of all atmospheric oxidation products of NO, including NO itself. The NO$_y$ speciation was studied during additional seasonal field campaigns. During these periods NO, NO$_2$, peroxycetyl nitrate (PAN), nitric acid (HNO$_3$) and particulate nitrate were measured. For this purpose, suitable analytical techniques were further developed. In particular, a technique for the measurement of HNO$_3$ and particulate nitrate with sufficiently high temporal resolution had to be found, since commonly used filter and denuder techniques require long sampling times followed by time-consuming off-line analysis.

First, a system for the quasi-continuous measurement of HNO$_2$, HNO$_3$ and particulate nitrate was built and characterized. The system consisted of a continuously operating denuder for gases coupled to an aerosol collector for particles. The analysis was performed automatically by ion chromatography after pre-concentration, and low detection limits (10 ppt) were achieved with a temporal resolution of 20 minutes. The first field campaign was conducted at the Dübendorf station of the Swiss National Monitoring Network for Air Pollution (NABEL). Relatively high HNO$_2$ concentrations of up to 3.2 ppb were especially remarkable at this site.

Second, NO$_y$ measurements were conducted during a summer field campaign at the Jungfraujoch. A key question was: How often is the station influenced by regional emission sources? It was found that NO$_y$ shows a diurnal cycle similar to the known diurnal variation of the aerosol surface area concentration. Due to different day and night concentrations, an estimate of the dilution of convective boundary layer air with free tropospheric air during
thermally induced vertical transport was made. In the third part of the study, the influence of different meteorological processes during different seasons on the NO$_y$ level and speciation was investigated. It was shown that föhn events, synoptical lifting (e.g. fronts) and thermally induced vertical transport have a strong influence on the NO$_y$ concentration and partitioning. The variability caused by meteorological processes often dominated the seasonal variability. As a result of meteorological analysis, it was possible to "filter" the data to obtain information about the undisturbed (i.e., virtually uninfluenced by anthropogenic pollution) free troposphere over the Alpine region. No previous studies or analysis of meteorological transport processes have been conducted in the Alpine region. Thus, present measurements at the JFJ have substantially added to the European database of NO$_y$ and constituent species. Finally, the Jungfraujoch data was used to estimate the export of PAN through thermally induced vertical transport. It was shown that thermal processes may add to the transport of reactive nitrogen compounds to the free troposphere and hence result in the long-range transport of air pollutants.
Zusammenfassung


In der vorliegenden Arbeit wurden während zwei Jahren Messungen von der Summe aller reaktiven Stickstoffverbindungen (NO\textsubscript{y}) an der hochalpinen Forschungsstation Jungfraujoch durchgeführt. Unter NO\textsubscript{y} versteht man alle atmosphärischen Oxidationsprodukte von NO, inklusive NO. Zusätzlich wurden zur Bestimmung von einzelnen NO\textsubscript{y}-Komponenten saisonale Messkampagnen durchgeführt. Während dieser Perioden wurde NO, NO\textsubscript{2}, Peroxyacetilnitrat (PAN), Salpetersäure (HNO\textsubscript{3}) und partikelförmiges Nitrat gemessen. Dazu war der Aufbau von geeigneten Analysemethoden notwendig. Insbesondere für die Messung von HNO\textsubscript{3} und partikelförmigem Nitrat musste eine geeignete Technik mit genügend hoher zeitlichen Auflösung gefunden werden, da die normalerweise eingesetzten Filter- und Denudertechniken lange Probenahmezeiten benötigen, einen sehr hohen Arbeitsaufwand bedingen und zudem Artefakte auftreten können.

Im ersten Teil der Arbeit wurde ein System zur quasi-kontinuierlichen Bestimmung von HNO\textsubscript{2}, HNO\textsubscript{3} und partikelförmigem Nitrat aufgebaut und weiterentwickelt. Dabei handelt es sich um einen kontinuierlich operierenden Denuder (für Gase) gekoppelt an einen Aerosolkollektor (für Partikel). Die Analyse wird dabei automatisch nach Aufkonzentrierung mittels Ionenchromatographie durchgeführt, wobei tiefe Nachweisgrenzen (10 ppt) bei einer zeitlichen Auflösung von 20 min erreicht werden. Eine erste Feldmessung wurde damit an der Station Dübendorf des Nationalen Beobachtungsnetzes für Luftfremdstoffe (NABEL) durchgeführt. Dabei sind insbesondere die relativ hohen Konzentrationen von HNO\textsubscript{2} bis 3.2 ppb bemerkenswert.

Im zweiten Teil der Arbeit wurden NO\textsubscript{y} Messungen während einer Sommerkampagne auf dem Jungfraujoch durchgeführt. Dabei stand die
1 Introduction

Concern for our air environment is not a new phenomena. Thus, in the 12th century the philosopher, scientist, and jurist Moses Maimoides (1135-1204) wrote [Finlayson-Pitts and Pitts, 1986]:

"Comparing the air of cities to the air of deserts and arid lands is like comparing waters that are befouled and turbid to waters that are fine and pure..."

Coal began to replace wood for domestic heating in the 13th century, with a dramatic impact on the air quality in cities. In the 17th century the so called "London smog" was described for the first time by the astrologer John Gadbury, who referred to it as "Great Stinking Fogs" [Brimblecombe, 1987]. In the 20th century, there was a renewed interest in air pollution and its health effects when a number of so-called killer smogs occurred. During the most severe episode in 1952 an excess number of 4000 deaths over that expected for the particular time of year and location was recorded in London. Very low inversion levels concentrated the pollutants in a relatively small volume, although the actual pollutants responsible for the fatalities have not been identified. However, the type of air pollution was characterized by very high SO2 and particle concentrations, and is known since then as London or sulfurous smog. Emission control, i.e. the use of fuel with a low sulfur content, reduced the SO2 emissions drastically in the 1980s. Photochemical air pollution has been a recognized problem in the US since the 1950s when plant injury symptoms were connected with gases produced during the irradiation of hydrocarbons and oxides of nitrogen [Haagen-Smit et
In the late 1950s peroxyacetyl nitrate (PAN) was discovered in long-path IR measurements of the Los Angeles smog (see Stephens [1987] for a discussion of early photochemical smog studies). In the 1960s and 1970s limited air quality monitoring began, and the "LA smog" problem was identified as a widespread phenomenon. By the mid-1970s, it had become clear that the major atmospheric phenomena air pollution, acid rain, airborne toxics, as well as the clean troposphere were linked in one continuous cycle. In this cycle, reactive nitrogen compounds, abbreviated as NOy, play a central role. Reactive nitrogen (NOy), is defined as the sum of NOx (NO + NO2) and its atmospheric oxidation products, abbreviated NO2. The chemical transformation occurring in the NOy family can be thought as a system of reactions wherein the major source species NO + NO2 are eventually oxidized to inorganic nitrate (HNO3 and particulate nitrate). Oxides of nitrogen are critical in determining atmospheric oxidation rates by influencing the photochemical production of ozone, and consequently, hydroxyl radical concentration in the troposphere [e.g. Crutzen, 1974; Roberts, 1995].

The system of reactions within the NOy family is systematically shown in Figure 1.1.

Fig. 1.1: Schematic representation of the NOy chemistry pertaining the troposphere (from Roberts [1995]).
The conversion of NO to NO₂ has a special significance to the chemistry of the troposphere. The NOₓ-O₃ photochemistry is often thought as a "photostationary state" involving the following three reactions:

\[
\begin{align*}
\text{NO} + \text{O}_3 & \rightarrow \text{NO}_2 + \text{O}_2 + \Delta H \\
\text{NO}_2 + h\nu & \rightarrow \text{NO} + \text{O}(^3\text{P}) \\
\text{O} + \text{O}_2 + \text{M} & \rightarrow \text{O}_3 + \text{M} + \Delta H
\end{align*}
\]

The net effect of these reactions is to convert sunlight to heat. It has been demonstrated from simultaneous measurements of NO, NO₂, O₃ and solar UV (e.g. Parrish et al., 1986) that the cycle represented by reaction (1.1)-(1.3) is not in balance during the daytime. The NO₉/NO ratio is always larger than it can be accounted for by this simple cycle. There are a number of reactions, in addition to (1.1), that convert NO to NO₂. Thus, the reactions

\[
\begin{align*}
\text{HO}_2 + \text{NO} & \rightarrow \text{NO}_2 + \text{OH} \\
\text{RO}_2 + \text{NO} & \rightarrow \text{NO}_2 + \text{RO}
\end{align*}
\]

will result in a net ozone production. The radicals HO₂ and RO₂ (where R is an organic group) are formed from the photo-oxidation of CO and organic compounds by OH radicals. The hydroxyl radical is the key to understanding tropospheric chemistry. It is formed by photolysis of ozone according to reactions (1.6) and (1.7).

\[
\begin{align*}
\text{O}_3 + h\nu & \rightarrow \text{O}(^1\text{D}) + \text{O}_2 \\
\text{O}(^1\text{D}) + \text{H}_2\text{O} & \rightarrow 2 \text{OH}
\end{align*}
\]

A further source of OH radicals is the photolysis of nitrous acid (HONO). HONO is mainly built up in polluted air masses during the night-time, although the formation mechanisms are not well characterized. A discussion of the HONO formation is given in Chapter 2.

The ultimate fate of NOₓ in the troposphere is the oxidation to HNO₃ and particulate nitrate and deposition either by wet or dry mechanisms. This
oxidation can occur directly through reaction (1.8)

\[
\text{NO}_2 + \text{OH} + M \rightarrow \text{HNO}_3 + M \quad (1.8)
\]

which is one of the key termination reactions for OH radicals in tropospheric chemistry. Another important pathway of the HNO₃ formation is the reaction of N₂O₅ with liquid water. N₂O₅ is formed by reaction of NO₂ with the NO₃ radical, which is formed itself by reaction of NO₂ with O₃. The NO₃ radical is an important oxidizing species of the night-time chemistry. Other loss mechanisms of NO₃ include the reaction with NO to reform NO₂ and the reaction with alkenes to form organic nitrates. The NO₃ radical is rapidly photolized during the daytime.

Another important NOy species is peroxyacetyl nitrate (PAN), which is formed from the reaction of acetyl radicals with O₂ and NO₂.

\[
\begin{align*}
\text{O} & + \text{O}_2 \rightarrow \text{O}_2\text{O}^* \\
\text{O}_2\text{O}^* & + \text{NO}_2 \quad \xrightleftharpoons{\Delta T} \quad \text{O}_2\text{O}^*\text{NO}_2
\end{align*}
\]

There are a variety of sources of the acetyl radical, including acetaldehyde oxidation by OH or NO₃, and atmospheric oxidation of ethane. The importance of PAN to the troposphere lies in its ability to reform NO₂ by thermal decomposition. PAN does not absorb radiation above 290 nm so it is not expected to photodissociate in the troposphere. Aqueous-phase scavenging is not expected to be an important tropospheric removal path for PAN either because it is not highly water-soluble. As a consequence PAN acts as an important reservoir for NOₓ, allowing for the long-range transport of NOₓ. The rate constant for decomposition of PAN, \( k_{-1.10} \), has been determined in several studies, and can be described by the following expression [Finlayson-Pitts and Pitts, 1986]:

\[
k_{-1.10} = 1.95 \times 10^{16} e^{-13.54/T} \text{ s}^{-1}
\]
Thus, the lifetime of PAN is highly temperature dependent. Table 1.1 summarizes rate constants and lifetimes for the thermal decomposition of PAN at various temperatures. It should be noted that these lifetimes will be only realized if the peroxyacetyl radical formed on the decomposition is removed rapidly compared to its reaction with NO₂ to reform PAN. This is the case in the presence of NO. Thus, at high NO₂/NO ratios and/or low temperatures, the decomposition reaction is inhibited and hence PAN can build up.

Table 1.1: Rate constants and lifetimes for the thermal decomposition of PAN [Finlayson-Pitts and Pitts, 1986].

<table>
<thead>
<tr>
<th>Temperature [°C]</th>
<th>rate constant (k_{1.10} [s^{-1}])</th>
<th>lifetime (\tau = 1/k_{1.10})</th>
</tr>
</thead>
<tbody>
<tr>
<td>-30</td>
<td>(1.2 \cdot 10^8)</td>
<td>2.6 yrs</td>
</tr>
<tr>
<td>-20</td>
<td>(1.1 \cdot 10^7)</td>
<td>105 days</td>
</tr>
<tr>
<td>-10</td>
<td>(8.4 \cdot 10^7)</td>
<td>14 days</td>
</tr>
<tr>
<td>0</td>
<td>(5.6 \cdot 10^6)</td>
<td>50 h</td>
</tr>
<tr>
<td>10</td>
<td>(3.2 \cdot 10^5)</td>
<td>8.6 h</td>
</tr>
<tr>
<td>20</td>
<td>(1.6 \cdot 10^4)</td>
<td>1.7 h</td>
</tr>
<tr>
<td>30</td>
<td>(7.6 \cdot 10^4)</td>
<td>22 min</td>
</tr>
<tr>
<td>40</td>
<td>(3.2 \cdot 10^3)</td>
<td>5 min</td>
</tr>
</tbody>
</table>

NOₓ, PAN and inorganic nitrate are considered to be the most abundant NOₓ compounds in the troposphere, while their relative abundance varies systematically: NOₓ is most abundant close to sources; PAN tends to be most abundant in regionally polluted air masses where there is more active organic photochemistry; and inorganic nitrate is most abundant in the more remote areas of the troposphere. While NO and NO₂ are measured at many measurement stations within air pollution control programs, speciated and total NOₓ are determined much less frequently. There is especially a significant uncertainty in the levels and speciation of NOₓ in the non-urban troposphere due to a lack of measurements [Carroll and Thompson, 1995].
1.1 NOy speciation and budget studies

To date, the majority of the studies of the speciation and the budget of NOy have been conducted at sites within North and South America [e.g. Buhr et al., 1990; Sandholm et al., 1994; Singh et al., 1994; Talbot et al., 1994] with an emphasis on less polluted locations and including some work over the Pacific Ocean and Hawaii [Atlas et al., 1992; Singh et al., 1996]. Information from Europe is far more limited [Solberg et al., 1997; Harrison et al., 1999]. The relative contribution of individual NOy species to the total has been an important subject of research in the past few years. Table 1.2 summarizes reported measurements of total NOy and constituent species.

The studies summarized in Table 1.2 were all performed in air masses of regional or remote character, either at surface measurement sites, or with aircraft based campaigns. It is apparent from Table 1.2 that the sum of individually measured NOy species is often less than measured total NOy (Σ(NOy)/NOy < 1) determined after catalytic conversion as NO at many sites. This so-called "shortfall" in NOy has both theoretical and instrumental implications. Possible interpretations of the NOy shortfall include the presence of reactive nitrogen compounds which are present in significant quantities but which are not measured in a given data set, interfering compounds (see section 1.3), and loss processes in inlet systems, e.g. adsorption of HNO3. NOy budget observations usually include measurements of NOx, PAN, HNO3 and particulate nitrate, and sometimes peroxypropionyl nitrate (PPN). PPN has relative abundances that range from a few per cent to 30% of PAN, and the PPN/PAN ratio was found to decrease systematically with the air mass age [Ridley et al., 1990]. Therefore, PPN may be an important constituent of total NOy especially close to source regions, whereas other PAN-type compounds seem to be less important. Other organic nitrates, i.e. alkyl nitrates, contribute only with a few ppt to the reactive nitrogen budget in the remote troposphere [e.g., Atlas et al., 1993]. Floke et al. [1998] found that the sum of alkyl nitrates (C1-C8) averaged 120 ppt at the Schauinsland station in the black forest, Germany.
Table 1.2: Partitioning and budget of NO\textsubscript{y} from different field studies.

<table>
<thead>
<tr>
<th>Location</th>
<th>Sampling period</th>
<th>NO\textsubscript{y}/NO\textsubscript{x}</th>
<th>PAN/NO\textsubscript{y}</th>
<th>HNO\textsubscript{3}/NO\textsubscript{y}</th>
<th>NO\textsubscript{3}/NO\textsubscript{y}</th>
<th>Σ(NO\textsubscript{y})/NO\textsubscript{y}</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Niwot Ridge, Colorado</td>
<td>5-8/84</td>
<td>0.29</td>
<td>0.16</td>
<td>0.10</td>
<td>0.02</td>
<td>0.58</td>
<td><em>Fahey et al.</em> [1986]</td>
</tr>
<tr>
<td>Colorado</td>
<td>summer 87</td>
<td>0.32</td>
<td>0.24</td>
<td>0.10</td>
<td>0.02</td>
<td>0.73</td>
<td><em>Ridley</em> [1991]</td>
</tr>
<tr>
<td>Scotia, Pen.</td>
<td>summer 86</td>
<td>0.59</td>
<td>0.14</td>
<td>0.16</td>
<td>0.04</td>
<td>0.93</td>
<td><em>Ridley</em> [1991]</td>
</tr>
<tr>
<td>Continental US, free troposphere</td>
<td>8-9/86</td>
<td>0.14</td>
<td>0.42</td>
<td>0.16</td>
<td>0.07</td>
<td>0.7</td>
<td><em>Ridley</em> [1991]</td>
</tr>
<tr>
<td>Pacific, free troposphere</td>
<td></td>
<td>0.32\textsuperscript{a}</td>
<td></td>
<td></td>
<td></td>
<td>0.9\textsuperscript{a}</td>
<td></td>
</tr>
<tr>
<td>Pacific, PBL\textsuperscript{b}</td>
<td>8-9/86</td>
<td>0.11</td>
<td>0.04</td>
<td>0.33\textsuperscript{a}</td>
<td>-</td>
<td>-</td>
<td><em>Ridley</em> [1991]</td>
</tr>
<tr>
<td>Mauna Loa, DS\textsuperscript{c}</td>
<td>5-6/88</td>
<td>0.13</td>
<td>0.07</td>
<td>0.42</td>
<td>0.09</td>
<td>0.71</td>
<td><em>Atlas et al.</em> [1992]</td>
</tr>
<tr>
<td>Mauna Loa, US\textsuperscript{c}</td>
<td>5-6/88</td>
<td>0.15</td>
<td>0.10</td>
<td>0.49</td>
<td>0.23</td>
<td>0.98</td>
<td><em>Atlas et al.</em> [1992]</td>
</tr>
<tr>
<td>Scotia, Pen.</td>
<td>7-8/88</td>
<td>0.38</td>
<td>0.20</td>
<td>0.29</td>
<td>-</td>
<td>0.90</td>
<td><em>Parrish et al.</em> [1993]</td>
</tr>
<tr>
<td>Whitetop, Ten.</td>
<td>8-9/88</td>
<td>0.56</td>
<td>0.17</td>
<td>0.34</td>
<td>-</td>
<td>1.09</td>
<td><em>Parrish et al.</em> [1993]</td>
</tr>
<tr>
<td>Bondville, Ill.</td>
<td>8/88</td>
<td>0.38</td>
<td>0.12</td>
<td>0.13</td>
<td>-</td>
<td>0.80</td>
<td><em>Parrish et al.</em> [1993]</td>
</tr>
<tr>
<td>North Bay, Ont.</td>
<td>7-8/90</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>0-2 km altitude</td>
<td></td>
<td>0.17</td>
<td>0.22</td>
<td>0.33</td>
<td>0.05</td>
<td>0.70\textsuperscript{d}</td>
<td><em>Singh et al.</em> [1994]</td>
</tr>
<tr>
<td>2-4 km altitude</td>
<td></td>
<td>0.09</td>
<td>0.43</td>
<td>0.22</td>
<td>0.05</td>
<td>0.77\textsuperscript{d}</td>
<td><em>Singh et al.</em> [1994]</td>
</tr>
<tr>
<td>4-6 km altitude</td>
<td></td>
<td>0.06</td>
<td>0.38</td>
<td>0.09</td>
<td>0.04</td>
<td>0.54\textsuperscript{d}</td>
<td><em>Singh et al.</em> [1994]</td>
</tr>
<tr>
<td>Goose Bay</td>
<td>7-8/90</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>0-2 km altitude</td>
<td></td>
<td>0.21</td>
<td>0.39</td>
<td>0.52</td>
<td>0.06</td>
<td>1.13\textsuperscript{d}</td>
<td><em>Singh et al.</em> [1994]</td>
</tr>
<tr>
<td>2-4 km altitude</td>
<td></td>
<td>0.15</td>
<td>0.77</td>
<td>0.29</td>
<td>0.04</td>
<td>1.19\textsuperscript{d}</td>
<td><em>Singh et al.</em> [1994]</td>
</tr>
<tr>
<td>4-6 km altitude</td>
<td></td>
<td>0.11</td>
<td>0.76</td>
<td>0.11</td>
<td>0.02</td>
<td>1.00\textsuperscript{d}</td>
<td><em>Singh et al.</em> [1994]</td>
</tr>
<tr>
<td>Izanía (Day)</td>
<td>7-8/93</td>
<td>0.15</td>
<td>0.04</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td><em>Fischer et al.</em> [1998]</td>
</tr>
<tr>
<td>Izanía (Night)</td>
<td>7-8/93</td>
<td>0.12</td>
<td>0.03</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td><em>Fischer et al.</em> [1998]</td>
</tr>
<tr>
<td>Pacific 35-45°N</td>
<td>2-3/94</td>
<td>0.09</td>
<td>0.36</td>
<td>0.42</td>
<td>-</td>
<td>0.87</td>
<td><em>Thompson et al.</em> [1997]</td>
</tr>
<tr>
<td>Jungfraujoch</td>
<td>summer 97</td>
<td>0.22</td>
<td>0.36</td>
<td>0.07</td>
<td>0.17</td>
<td>0.82</td>
<td>this work</td>
</tr>
<tr>
<td>Jungfraujoch</td>
<td>winter 98</td>
<td>0.46</td>
<td>0.20</td>
<td>0.09</td>
<td>0.03</td>
<td>0.78</td>
<td>this work</td>
</tr>
</tbody>
</table>

\textsuperscript{a}Ranges indicate two different HNO\textsubscript{3} measurement techniques.

\textsuperscript{b}PBL, Planetary Boundary Layer.

\textsuperscript{c}DS, down-slope winds; US, up-slope winds.

\textsuperscript{d}(NO\textsubscript{y}), excluding particulate nitrate.
The average contribution of alkyl nitrates to total NO$_y$ was $\sim$3%, with little seasonal variation. Another important NO$_y$ species is HONO (see also Chapter 2). However, it is rapidly photolized at wavelengths $<$400 nm during the daytime hours to yield OH radicals. Therefore, HONO is mainly of importance in urban atmospheres, whereas the mixing ratios at remote locations tend to be very low [Lammel and Cape, 1996].

**Aircraft based NO$_y$ measurements**

Measurements of trace gases in the middle and upper troposphere are often performed by aircraft. These measurements cover usually only a short temporal range. Nevertheless, they are often the only possibility to study the middle and upper troposphere.

Results of several airborne field campaigns have been published. Arctic air masses in the lower troposphere were sampled during the Arctic Boundary Layer Experiments (ABLE 3A+B) [Sandholm et al., 1992, 1994; Singh et al., 1992, 1994; Talbot et al., 1994]. Concentrations of NO$_y$ increased from a median of 350 ppt at low altitudes to 600 ppt at higher altitudes [Sandholm et al., 1992]. The largest single component at the highest altitudes measured (6 km) was PAN and its increase with altitude explained the increase in NO$_y$. During the Pacific Exploratory Missions (PEM A+B) [Jaffe et al., 1996; Koike et al., 1996; Thompson et al., 1997] extensive measurements of total and known individual nitrogen species were made over the Pacific Ocean. In contrast to ABLE 3A+B, only weak vertical NO$_y$ concentration gradients were observed. However, a significant variation in the NO$_y$ composition was observed for air masses with different origin. Partitioning of reactive nitrogen in the continental air was characterized by higher NO$_x$/NO$_y$ and PAN/NO$_y$ ratios than observed in maritime and tropical air. A rapid increase of the PAN/NO$_y$ ratio from $\sim$0.04 to $\sim$0.20 was observed in maritime and tropical air at altitudes between 3 and 5 km.

**NO$_y$ measurements at surface stations**

Besides aircraft-based campaigns, the data of high mountainous measurement stations are used to study the troposphere between 2 and 4 km asl. However, only very few time series of NO$_y$ and NO$_z$ species are
available from such stations. An exception is the Mauna Loa Observatory, 3400 m asl, Hawaii, where ongoing CO₂ measurements started in 1956. These measurements were accomplished by many other parameters including NO₂ species with time [e.g. Atlas et al., 1992; Atlas and Ridley, 1996, Ridley et al., 1998]. The Mauna Loa observatory data showed that time series of mountainous stations have to be carefully evaluated in terms of local meteorological influence on the station. A diurnal upslope-downslope flow pattern was recognized many years ago [Mendonça, 1969]. Transport to Mauna Loa is governed largely by subtropical anticyclones and synoptic scale disturbances. Island scale transport is driven by radiative heating and cooling of the lava surface, resulting in near-surface winds with a bimodal distribution. Upslope winds are observed during sunlit hours, and near sunset the collapse or subsidence of air that was convectively mixed during the afternoon from lower altitudes to altitudes above the station is readily observed. As a consequence background data were restricted to the hours 0000-0800 [Bodhaine, 1983] or 2100-1000 local standard time (LST) [Atlas et al., 1992].

The partitioning and budget of NO₂ at the Mauna Loa Observatory is shown in Table 1.2, along with measurements from other mountainous stations. PAN contributed on average only 7-10% to total NO₂, which is typical for tropical air masses due to the temperature dependent decomposition of PAN. Nitric acid was the most abundant NO₂ species at the Mauna Loa and dominated over particulate nitrate. However, a factor of 3 difference was observed in the NO₃/NO₂ ratio for up- and downslope conditions [Atlas et al., 1992]. The high levels of particulate nitrate during upslope periods were often associated with increases in aerosol Na⁺ and NH₄⁺ from the marine boundary layer. Further investigations concerning concentration gradients and dry deposition of HNO₃ at the Mauna Loa Observatory were described by Lee et al. [1993]. They reported high dry deposition velocities ranging from 0.27 to 4 cm s⁻¹ and concluded that free tropospheric HNO₃ mixing ratios may be underestimated by 20% at the Mauna Loa Observatory. A springtime maximum of PAN, NOₓ and ozone was reported by Ridley et al. [1998]. PAN was a factor of 4.1 higher at Mauna Loa compared to summer data. However, variations over periods of a few days to weeks were often larger
than the seasonal amplitude. Measurements at Spitzbergen in the Norwegian Arctic showed also a springtime PAN maximum with a factor >3 difference between winter and late March [Solberg et al., 1997]. PAN was the major NOy component at Spitzbergen, whereas HNO₃ was present at very low mixing ratios (5-20 ppt). Another mountainous station with recent NOy measurements is Izaña, 2370 m asl, Tenerife [Fischer et al, 1998]. However, no NOy budget information is available from this site because no inorganic nitrate was measured. The PAN/NOy ratio was with average values of 0.03 to 0.04 very low, indicating that the station received air masses of tropical origin. Similar to Mauna Loa, a very pronounced diurnal cycle was observed at the Izaña station, with maximum NOy concentrations around noon. This was attributed to topographically induced wind systems with an upslope flow of polluted air during the daytime (0900-1800 LST). The variations of the chemical composition of different air masses was therefore studied with nighttime data from this station, which have been considered to represent free tropospheric (FT) air. A comparison of these data with FT data from the Mauna Loa Observatory showed similar concentrations for most trace gases, while significant differences were obvious during the daytime hours. This can be explained by the presence of more local sources at Tenerife, and by the lower elevation of the Izaña station.

1.2 The high-alpine research station Jungfraujoch

For the present study, we made measurements of total and speciated NOy at the high-alpine research station Jungfraujoch, Switzerland. The Jungfraujoch (JFJ) research station and a topographical model with prevailing wind directions is shown in Figures 1.2 and 1.3.
The high-alpine research station JFJ (46°33'N, 7°59'E) is located in the Sphinx observatory at 3580 m asl on the main crest of the Bernese Alps and is surrounded by glaciers and rocks. Due to its location on a crest between two mountain tops, the local wind direction shows a bimodal distribution with prevailing winds from the north-west and the south-east (see Figure 1.3). Being the highest railway station in Europe (built 1896-1912), it is easily accessible by train throughout the year. With the exception of occasional construction activities, local emissions from the station and the tourist facilities are low since all heating is electrical and waste is sent back to the valley. The first research activities started in the 1920s with astronomical observations, and the JFJ research station was founded in 1932. Scientific activities are co-ordinated by the international foundation high-alpine research stations JFJ and Gornergrat (HFSJG). The JFJ became part of the Swiss National Air Pollution Monitoring Network (NABEL), which has been operated by EMPA Dübendorf on behalf of the Swiss Agency for Environment, Forests and Landscape (BUWAL) since 1981. Furthermore, the
JFJ high-alpine station has been the site of an aerosol program since 1988 [Baltensperger et al., 1997; Lugauer et al., 1998; Nyeki et al., 1998]. Due to the importance of monitoring long-term trends of gaseous and aerosol parameters in the remote troposphere, the JFJ station has been incorporated into the Global Atmosphere Watch (GAW) program of the World Meteorological Organization (WMO). The JFJ is part of the combined European GAW virtual baseline station, additionally comprising the Zugspitze (2962 m, Germany) and Sonnblick (3106 m, Austria) high-alpine stations. Ongoing measurements of NO\textsubscript{y} started in March 1997 at the JFJ and were accompanied by seasonal measurement campaigns of speciated NO\textsubscript{y}.

**Diurnal and seasonal variation of aerosol parameters at the Jungfraujoch**

Studies of the remote troposphere over Central Europe can only be achieved by aircraft or at high Alpine measurement stations. However, the situation at Alpine locations such as the JFJ is completely different from that of relatively isolated mountainous sites such as Izaña and Mauna Loa. First, the situation in the center of Europe with its large industrialization and population and hence high air pollution levels may have a strong influence on the air quality at such stations. Second, the Alpine area is geographically more complex compared to other mountainous stations, where a simple time window is
often sufficient to distinguish between "clean" FT conditions and pollution events.

It is therefore crucial to know the processes which possibly influence the JFJ measurement station. Thermally induced vertical transport has been recognized as an important mechanism of upward transport at the JFJ [Baltensperger et al., 1997]. Figure 1.4 shows the seasonal variability of the diurnal variation of the aerosol surface area concentration for specific meteorological situations described in Lugauer et al. [1998]. The seasonal variation in the aerosol surface area concentration and other aerosol parameters is described in Nyeki et al. [1998].

![Fig. 1.4: Seasonal variability of the diurnal variation of the aerosol surface area concentration (after Lugauer et al. [1998])](image)

It can be seen that a strong diurnal variation of the aerosol surface area is observed during the spring and summer months. This thermally induced vertical transport causes on average increased aerosol surface area concentrations during the summer, resulting in a pronounced seasonal variation of the aerosol surface area concentration. Based on these findings, the key questions for this work were:
• Is the NOy composition at the JFJ governed by chemical transformation within the NOy family, or by meteorological transport?

• What are the transport mechanisms which govern the NOy concentration at the JFJ?

• What are the consequences of this transport for the free troposphere? Is there a significant export of reactive nitrogen to the FT?

These questions can be simplified as "What is measured at the JFJ?". To know the answer is of great importance not only for the interpretation of the present data set, but also for future work.

1.3 Measurement techniques for NOy and constituent species

This section gives a short overview of different measurement techniques for total and speciated NOy. Details of the instrumentation used at the JFJ is given in Chapter 2.2 and 3.2. A summary of different analytical methods is shown in Table 1.3.

NO and NOx measurement

Chemiluminescence from the reaction with O3 has become the standard technique for the measurement of NO. The light-emitting species is electronically excited NO2. NOx is usually measured by converting it first to NO, followed by chemiluminescence. Mainly heated molybdenum catalysts or photolytical conversion are used to reduce NO2 to NO. It should be noted that there is still a sizable body of NO2 data determined after conversion on heated molybdenum. Caution must be exercised in drawing conclusions from these measurements, because surface converters can convert other reactive nitrogen species such as PAN to NO, resulting in substantial positive biases for NO2.
Table 1.3: Summary of techniques used to measure NO$_y$ and constituent species.

<table>
<thead>
<tr>
<th>Technique</th>
<th>Det. Limit</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>NO Chemiluminescence</td>
<td>5 ppt</td>
<td><em>Fahey et al.</em> [1986]</td>
</tr>
<tr>
<td>Differential Optical Absorption Spectroscopy (DOAS)</td>
<td>400 ppt</td>
<td><em>Platt and Perner</em> [1982]</td>
</tr>
<tr>
<td>NO$_2$ Chemiluminescence (NO+O$_3$) after reduction on Mo catalyst or photolytical conversion</td>
<td>10 ppt</td>
<td><em>Fahey et al.</em> [1986]</td>
</tr>
<tr>
<td>DOAS (5 km pathlength)</td>
<td>80 ppt</td>
<td><em>Platt and Perner</em> [1982]</td>
</tr>
<tr>
<td>Tunable Diode Laser Spectroscopy (TDLS)</td>
<td>125 ppt</td>
<td><em>Fehsenfeld et al.</em> [1990]</td>
</tr>
<tr>
<td>(TDLS)</td>
<td>20 ppt</td>
<td><em>Schiff et al.</em> [1990]</td>
</tr>
<tr>
<td>Σ NO$_y$ Chemiluminescence (NO+O$_3$) after reduction on Mo or Au catalyst</td>
<td>&lt;20 ppt</td>
<td><em>Fahey et al.</em> [1986]</td>
</tr>
<tr>
<td>PAN GC with electron capture detection</td>
<td>15 ppt</td>
<td><em>Schrimpf et al.</em> [1995]</td>
</tr>
<tr>
<td>TDLS</td>
<td>300 ppt</td>
<td></td>
</tr>
<tr>
<td>HNO$_2$ DOAS</td>
<td>200 ppt</td>
<td><em>Lammel and Cape,</em> [1996]</td>
</tr>
<tr>
<td>Denuder (Na$_2$CO$_3$ / glycerol)</td>
<td>2 ppt</td>
<td><em>Li</em> [1994]</td>
</tr>
<tr>
<td>Wet effluent diffusion denuder / IC</td>
<td>10 ppt</td>
<td>This work</td>
</tr>
<tr>
<td>HNO$_3$ TDLS</td>
<td>75 ppt</td>
<td><em>Schiff et al.</em> [1990]</td>
</tr>
<tr>
<td>Filter pack (Teflon / Nylon)</td>
<td>2 ppt</td>
<td><em>Williams et al.</em> [1997]</td>
</tr>
<tr>
<td>Denuder (NaCl)</td>
<td>2 ppt</td>
<td><em>Li</em> [1994]</td>
</tr>
<tr>
<td>Wet effluent diffusion denuder / IC</td>
<td>10 ppt</td>
<td>This work</td>
</tr>
<tr>
<td>Nitrate Filter pack (Teflon / Nylon)</td>
<td>2 ppt</td>
<td><em>Williams et al.</em> [1997]</td>
</tr>
<tr>
<td>Wet effluent diffusion denuder / aerosol collector / IC</td>
<td>10 ppt</td>
<td>This work</td>
</tr>
</tbody>
</table>

Spectroscopic methods such as TDLS or DOAS can be alternative techniques with the exception of remote locations due to their higher detection limits.
Measurement of total NO$_y$

Total reactive nitrogen is usually measured after conversion to NO with chemiluminescence technique. The conversion is performed on either gold or molybdenum catalysts, heated to >300°C. Most of the above NO$_y$ field studies were performed with gold (300-350°C) as a catalyst for the reduction of total NO$_y$, with addition of 0.2-5% carbon monoxide as a reducing agent. This technique seems to yield highest conversion efficiencies and shows lowest interference of non-NO$_y$ species. However, it should be noted that this method does not convert particulate nitrates with a low volatility (e.g. NaNO$_3$), which may be important in maritime air masses.

Discrepancies in NO$_y$ measurements have been a topic of discussion since two different instruments showed significant disagreement during PEM West A [Crossley, 1996]. NO$_y$ was often by a factor 2 or more greater than the sum of its individually measured components. The difference between the instruments was attributed to the conversion of several non-NO$_y$ species, including HCN and NH$_3$, under some conditions. As a consequence, a laboratory study involving different NO$_y$ converters operating under various conditions was done by Kliner et al. [1997]. They investigated the conversion efficiencies as a function of pressure and catalyst temperature, and as a function of reducing-agent concentrations for both H$_2$ and CO. Furthermore, the effect of humidity and ozone on the conversion efficiencies was investigated. They found high conversion efficiencies of HCN and NH$_3$ for their converters under conditions typically employed in the field (i.e. catalyst temperature 300°C, H$_2$ or CO as a reducing agent). This finding is important for the interpretation of the NO$_y$ shortfall, since e.g. HCN is well mixed throughout the major part of the troposphere, with a mixing ratio of ~170 ppt. However, the converters described by Kliner et al. [1997] were all operated at low pressure (<330 hPa). The pressure of the converter used at the JFJ was regulated to 600 hPa, and no conversion of NH$_3$ was observed. This is in line with results of a similar converter described by Feigl [1998], where no conversion of NH$_3$ and N$_2$O was observed. Feigl [1998] investigated also the interference of HCN and found conversion between 2 and 10% at a catalyst temperature of 300°C. However, operating the converter at 360°C resulted in 20-35% conversion of HCN.
**PAN measurement**

PAN is routinely monitored using gas chromatography with electron capture detection. Calibration of the GC requires generating and injection of known PAN concentrations into the GC. This was performed by the photolysis of excess acetone and NO in zero air, according to reaction 1.11.

\[
\text{hv, O}_2 \rightarrow \text{hv, O}_2, \text{NO} \]

NO was used as the concentration-determining compound. This allowed PAN measurements to be directly linked to the NO standard.

**HONO, HNO\textsubscript{3} and particulate nitrate measurements**

HONO measurements by DOAS have been performed with success in many case studies. However, spectroscopic techniques for the measurement of HONO and HNO\textsubscript{3} often suffer from low sensitivity. In addition to spectroscopic techniques, HONO and HNO\textsubscript{3} have been determined by two other methods – diffusion denuder technique and filter technique. These methods have low detection limits but require relatively long sampling intervals. Furthermore, filter measurements of HONO and HNO\textsubscript{3} require a prefilter to remove particulate species, and the technique is susceptible to certain positive and negative artifacts [Appel and Tokiwa, 1981]. On a teflon filter, particulate NH\textsubscript{4}NO\textsubscript{3} can volatize into HNO\textsubscript{3} and NH\textsubscript{3} resulting in a significant positive HNO\textsubscript{3} error.

An alternative method for the measurement of HONO, HNO\textsubscript{3} and particulate nitrate is the wet effluent diffusion denuder / aerosol collector (WEDD/AC) technique coupled to ion chromatography. This technique was used for the measurement of HNO\textsubscript{3} and particulate nitrate at the JFJ, and instrumental details are described in chapter 2 along with several performance tests and the optimization of the denuder for HONO measurements. Further performance test done after this work are summarized in Chapter 5.
1.4 References


2 NO$_y$ Speciation with a Combined Wet Effluent Diffusion Denuder - Aerosol Collector Coupled to Ion Chromatography

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C. Zellweger$^{1,2}$, M. Ammann$^1$, P. Hofer$^2$, U. Baltensperger$^1$$^*$

$^1$Paul Scherrer Institute, CH-5232 Villigen PSI, Switzerland
$^2$EMPA, CH-8600 Dübendorf, Switzerland

Abstract

A wet effluent denuder / aerosol collector (WEDD/AC) system coupled to ion chromatography for the measurement of atmospheric HONO, HNO$_3$ and particulate nitrite, nitrate and sulfate is described. Several experiments were performed to outline its performance. The main features are low detection limits and a fast response to concentration changes which enables measurements with high time resolution. In contrast to highly soluble gases, the collection efficiency of less soluble gases is shown to depend on the Henry's law constant rather than on the uptake kinetics. To improve the collection efficiency for HONO under simultaneous presence of acidifying gases, NaHCO$_3$ was added to the effluent solution. The system was tested in a field campaign in the suburban area of Zürich, Switzerland. Elevated concentrations of nitrous acid up to 3.2 ppb were detected during the measurement campaign. The diurnal variation of the HONO to NO$_2$ ratio

2
clearly points to a fast and persistent process producing HONO in the atmosphere. The correlation with NOx and black carbon suggests a heterogeneous formation of HONO, and is consistent with a reaction on soot aerosol particle surfaces postulated from previous laboratory results.

2.1 Introduction

Reactive nitrogen plays a central role in the chemistry of the troposphere. It is involved in the production of atmospheric acidity and ozone on regional and global scales. Therefore a detailed knowledge of the sources, the chemical processes and the removal of reactive nitrogen is important for the understanding of atmospheric chemistry. Reactive nitrogen, abbreviated NOy, is defined as the sum of NOx and all compounds that are atmospheric oxidation products of NOx. The sum of the products of the NOx oxidation, abbreviated NOz, is defined as NOz = NOy-NOx. The emissions of reactive nitrogen occur as NO and NO2. Acidic and oxidizing conditions in the troposphere lead to the formation of nitric acid (HNO3), particulate nitrate and peroxycetyl nitrate (PAN). These species are considered to be the most abundant NOy compounds in the remote troposphere. A detailed overview of these compounds as well as other minor contributors to the NOy chemistry is given by Roberts [1995].

Especially in urban and polluted areas, nitrous acid (HONO) has been recognized as an important species of total reactive nitrogen (NOy) in the atmosphere. In heavily polluted areas highly elevated concentrations of HONO up to 14 ppb were detected [Appel et al., 1990]. The main importance of HONO lies in its photolysis to create the hydroxyl radical (at wavelengths λ = 290-400 nm) and hence its strong influence on the photochemical activity of polluted air masses.

To improve our understanding of the interplay between transport processes and chemical reactions of these pollutants, analytical methods with a fast response to concentration changes are crucial. However, reliable measurements of NO2 species at ambient concentrations are difficult to perform. The measurement of atmospheric nitric and nitrous acid and particulate nitrate is usually performed by filter and conventional denuder
techniques. These methods usually lack time resolution and are subject to many artifacts. For example, the loss of ammonium nitrate on filter samples due to evaporation is a well-known problem in the analysis of atmospheric aerosols [e.g. Appel and Tokiwa, 1981]. On basic filters, nitric acid is converted to nitrate. During conventional sampling of HONO on filters or denuders, nitrite can easily be oxidized to nitrate. Therefore, in-situ and on-line techniques are required for ambient HONO measurement. Spectroscopic methods such as FTIR, DOAS and TDLS usually require long pathways and often lack in sensitivity or suffer from interference (e.g. water vapor). However, they have been used successfully for monitoring HONO in heavily polluted areas [e.g. Appel et al., 1990]. An alternative method is the wet effluent diffusion denuder (WEDD) technique. It has been used for the measurement of atmospheric trace gases at ppb/ppt concentrations [Keuken et al., 1988; Neftel et al., 1996] and has been shown to allow a diffusion-based collection with discrimination of gaseous analytes from their particulate counterparts. In comparison to conventional coated denuders, WEDD allows measurements with a time resolution of a few minutes as well as immediate, quasi on-line analysis of the denuder effluent without any further treatment or dilution. After the removal of the gaseous species, the soluble fraction of particulate matter can be sampled with an aerosol collector (AC) by means of steam injection. The main advantages of this technique are low detection limits of a few ng m$^{-3}$ and a low artifact risk.

The design of existing systems considered collection of highly soluble gases with fast kinetics of the gas liquid transfer, where gas phase diffusion is the process controlling the collection efficiency in the WEDD. However, the collection efficiency may often depend on Henry's law rather than the uptake kinetics. Therefore, the concomitant collection of acidifying gases, e.g. HNO$_3$ or SO$_2$, has a strong influence on the collection of other species, such as HONO. This effect will be demonstrated in a field campaign and was the basis for the improvements of the WEDD system presented here. In addition, the field data on the aerosol inorganic composition HNO$_3$ and HONO show, for the first time, a close relationship of HONO to black carbon data pointing to soot as a possible substrate for HONO formation.
2.2 Experimental

Wet effluent denuder/aerosol collector coupled to ion chromatography

The WEDD technique is described in detail by other authors [Simon et al.; 1991, Simon and Dasgupta, 1993, 1995a, 1995b; Dasgupta et al. 1997]. The principle of the WEDD/AC-system is illustrated in Fig. 2.1.

![Diagram of WEDD/AC-system](image)

A constant air flow of typically 5 l min\(^{-1}\) is drawn through a parallel plate diffusion denuder. The parallel plate denuder (PPD) design we used was originally developed and described by Vecera and Dasgupta [1991a] and Blatter et al. [1994] and is basically a pressed quartz glass tube of 50 cm length. The active denuder surface area (parallel part) is 240 cm\(^2\), with a distance of 2 mm between the plates. The glass was coated with Na\(_2\)SiO\(_3\) using a procedure developed by Blatter (personal communication, 1996) which enabled a homogeneous water film on the denuder surface. Ultra pure water (18 M\(\Omega\)) is added with a peristaltic pump (Ismatec MS-CA 4/820, 0.30 ml min\(^{-1}\)). A similar device is described by Oms et al. [1996]. The aerosol collector consists of a thermally isolated 500 ml glass chamber where water vapor is added through a heating coil (300°C). The
supersaturation resulting from the mixing of the two flows causes aerosol particles to grow into droplets. At the chamber outlet, a cooling device (peltier element, Melcor CP2-127-06L, 2°C) mounted on a stainless steel maze leads to further steam condensation. The water droplets can then be separated from the air with an impactor. Both denuder effluent and aerosol collector water are alternately preconcentrated on ion exchange columns (Dionex AG4A-SC 4 mm) and afterwards automatically analyzed by ion chromatography (Sykam S1100, S3110, Dionex column AS4A-SC 4 mm) using 1.7 mM NaHCO₃ / 1.8 mM Na₂CO₃ as eluent. The duration of the preconcentration was 10 minutes.

**Particle generation and measurement**

In order to test the performance of the aerosol collector, ammonium nitrate and ammonium sulfate particles were generated using a nebulizer (TSI) followed by a diffusion dryer. The particle number concentration and size distribution were either measured by an optical particle counter (OPC) (LAS-X, Particle Measurement Systems) or by a scanning mobility particle sizer (SMPS). The SMPS system consisted of a differential mobility analyzer (DMA, TSI 3071A) combined with a condensation nucleus counter (CNC, TSI 3022). The DMA was operated with a total flow rate of 3.3 l min⁻¹, and the data acquisition was performed using the SMPS software.

**HONO source**

The collection efficiency of the WEDD was tested with an artificial HONO source. Production of HONO was performed via reaction of sodium nitrite with excess sulfuric acid. The flow reactor that was used has already been published elsewhere [Taira and Kanda, 1990] and was shown to yield stable HONO concentrations as low as 2 ppb [Ammann et al., 1997]. This source was preferred to the one described by Vecera and Dasgupta [1991b] because here no NH₃ was formed as a byproduct, which via its basicity can influence the collection efficiency (see below).
Field campaign
The measurements of the field campaign were performed at Dübendorf (430 m asl), a town located in the suburban area of Zürich, Switzerland. The area is covered by a dense network of roads with heavy traffic. The whole region is densely populated, and both industry and agriculture are present. The measurements of NO$_x$, CO and black carbon (BC) were performed with commercially available instruments. NO$_x$ (Monitor Labs 8841) and CO (Horiba APMA-360) were continuously measured within the Swiss national network of air pollution monitoring (NABEL). During April 1997, additional BC measurements were carried out with an aethalometer (GIV AE-10).

2.3 Results and Discussion

Performance of the denuder
The performance of the WEDD technique was partly described by Simon et al. [1991], Simon and Dasgupta [1993] and Blatter et al. [1994]. The effect of interfering compounds such as NO, NO$_2$ and PAN has been shown to be negligible [see also Neftel et al., 1996] and was confirmed to be less than 0.1 % for NO$_2$ concentrations up to 318 ppb by our experiments. The interference is therefore insignificant relative to the observed HONO concentrations. To characterize the WEDD in more detail, we mainly focused on the penetration of aerosol particles through the denuder and the collection efficiency for gaseous compounds.

To test the penetration of particles through the denuder, a steady flow of ammonium nitrate particles in air was delivered to the denuder, and the particle number concentration and size distribution for particles with a diameter $d \geq 0.1 \mu$m was measured before and after the wet and dry denuder with the OPC. Ammonium nitrate particles were chosen because of their hygroscopic property and hence their tendency to grow at low relative humidity. For both dry and wet denuder surfaces, no considerable loss of particles was found (penetration $101.3 \pm 5.2$ % dry, $103.4 \pm 5.1$ % wet). The major part of the uncertainty was caused by the instability of the particle
generation and, in addition, by the growth of small particles to a size detected by the OPC (d ≥ 0.1 μm) under humid conditions.

Since WEDDs are used for the measurement of atmospheric HONO and HNO₃, the collection efficiency $\varepsilon$ of the denuder is of great importance for the quantification of these species. Many papers already addressed the collection efficiency assuming that $\varepsilon$ is only limited by diffusion [e.g. Simon and Dasgupta, 1993, 1995]. For a PPD design the collection efficiency can then be described [De Santis, 1994] as

$$
\varepsilon = 1 - 0.91 \cdot \exp \left[ -15.08 \cdot \frac{\pi D L (2a + b)^2}{4 Q ab} \right]
$$

(1)

where $D$ is the diffusion coefficient of the gas, $L$ is the length of the tube, $a$ and $b$ are the short and long dimensions of the denuder cross section and $Q$ is the volumetric flow rate, respectively. Note that equation (1) contains a correction of the original formula by Ali et al. [1989], resulting in a slightly higher collection efficiency. For the present PPD design, equation (1) gives a collection efficiency $\varepsilon$ of > 99.9 % (at a flow rate of 5 l min⁻¹).

The transfer of gases to the aqueous phase of the effluent solution includes diffusion to the walls, accommodation to the surface, solvation into solution followed by dissociation and/or acid/base reactions. The uptake coefficient, $\gamma$, which lumps together accommodation, solvation and reaction, determines whether the mass transfer to the walls is diffusion controlled or not. For $\gamma > 0.01$, equilibration between gas and aqueous phase is established very rapidly, and mass transfer is therefore diffusion controlled [Msibi et al., 1993]. This is the case for HNO₃ [$\gamma = 0.07-0.11$, Van Doren et al., 1990, Ponche et al., 1993] as well as for HONO [$\gamma = 0.05$, Bongartz et al., 1994]. Thus, the collection efficiency mainly depends on the Henry's law constant, and $\varepsilon$ can be calculated as

$$
\varepsilon = \frac{c_a \cdot f_a}{c_a \cdot f_a + c_g \cdot f_g}
$$

(2)

where $c_a$ and $c_g$ are the concentrations [g cm⁻³] in the aqueous and gaseous phase and $f_a$ and $f_g$ are the flow rates [ml min⁻¹] in the aqueous and gaseous
phase, respectively. Substitution with the dimensionless Henry constant 
\( H^1 = c_{\text{d}}/c_g \) [Sander, 1996] leads to a collection efficiency given by

\[
\varepsilon = \frac{f_0}{f_0 + f_a} \quad (3)
\]

For molecules where acid/base reactions are involved, the effective Henry constant \( H_{\text{eff}} \) [Seinfeld 1986] has to be taken into account, defined as

\[
H_{\text{eff}} = H^1 \cdot \left( 1 + \frac{K_a}{[H^+]} \right) \quad (4)
\]

where \( K_a \) is the dissociation constant. Figure 2.2 shows the calculated collection efficiency for HNO\(_3\) and HONO, neglecting concentration gradients in the gas and liquid phase at the exit of the denuder.

![Graph showing calculated and measured denuder efficiency](image)

Fig. 2.2: Calculated denuder collection efficiency for HONO and HNO\(_3\) as a function of the denuder effluent pH, and experimentally observed efficiency for HONO.
To simulate a certain pH of the aqueous solution at the exit of the wet effluent denuder, various amounts of nitric acid were added to the water that was pumped into the denuder, while the gaseous HONO concentration from the HONO source was kept constant (2.6 ppbv). The pH resulting from the acid added to the water and the HONO uptake in the denuder was measured with a pH electrode after sampling the denuder effluent solution and is given in the experimental data points of Fig. 2.2. For the calculation of the theoretical collection efficiency, a Henry constant $H = H^1 / RT$ of 49 M atm$^{-1}$ for HONO was used [Schwartz and White, 1981]. It is obvious that the uptake efficiency of HONO is strongly dependent on the pH value of the denuder effluent. Adding small amounts of NaHCO$_3$ to the denuder water supply improves the uptake of HONO significantly and thus enables a quantitative detection of HONO. A NaHCO$_3$ concentration of 0.048 mM (4 mg l$^{-1}$, pH 7.9) has been found to be best suited for HONO detection in relatively clean air. Preconcentration of the denuder effluent on the ion exchange columns is still possible (see Chapter 2.2). However, the amount of NaHCO$_3$ added to the denuder effluent should be carefully evaluated in terms of the pollution characteristics of a certain measurement site. It might be necessary to add higher amounts of NaHCO$_3$ in highly polluted areas when acidic conditions dominate.

**Characterization of the aerosol collector**

The interference of NO$_2$ in the aerosol collector was found to be highly variable between 0.2 and 1 % of the incoming NO$_2$ (at 4 l min$^{-1}$). The interference may depend on trace gas compounds as well as aerosol concentration, which governs the number of droplets in the mist chamber. A correction of 0.6 % of the incoming NO$_2$ was made for the aerosol collector part of the HONO data (see below).

To test the collection efficiency, the aerosol collector was fed with a constant flow of ammonium sulfate particles which were produced by nebulizing an aqueous ammonium sulfate solution. In this case, (NH$_4$)$_2$SO$_4$ was chosen because of its relatively high deliquescence point (79.9% RH at room temperature, Tang and Munkelwitz, 1993). The particle concentration and size distribution were measured before and after the aerosol collector with an
SMPS. Figure 3 summarizes the collection efficiency as a function of the aerosol number concentration. A collection efficiency of 99.3 % was found for a particle number concentration of 11000 cm$^{-3}$. This number concentration corresponds to a mass concentration of 82 μg/m$^{-3}$ (at a mean diameter of 100 nm) and thus the collection efficiency is in qualitative agreement with Simon and Dasgupta [1995].

![Graph showing collection efficiency as a function of particle number concentration.

Fig. 2.3: Collection efficiency of the aerosol collector as a function of the particle number concentration (ammonium sulfate, polydisperse aerosol with a modal mobility diameter of 70 nm). Ambient aerosol concentrations in the mass relevant size range ($d \geq 100$ nm) are usually below 10000 cm$^{-3}$.

Ambient aerosol concentrations rarely exceed 10000 cm$^{-3}$, especially when only those particles with a significant mass contribution are considered, see, e.g. Hering et al. [1998]. Therefore the collection efficiency is by far sufficient for ambient aerosol analysis. Under conditions where very high aerosol concentrations are present, a quantitative collection efficiency can still be maintained by increasing the steam introduction rate. The collection efficiency is not only dependent on the number concentration but also on the particle diameter. With the measured size distributions, an estimate of the collection efficiency as a function of the particle diameter was performed. For
an overall collection efficiency of 99.1 % for an aerosol concentration of 33000 cm\(^3\), larger particles \((d \geq 200 \text{ nm})\) were collected to 100 %, and even very small particles \((d = 20 \text{ nm})\) were collected with over 95 % efficiency.

To compare the aerosol collector with other techniques, ammonium sulfate aerosol particles were sampled alternatively on teflon filters (pore size 1 \(\mu\text{m}\)), and the filters were then analyzed by IC after ultrasonic extraction in ultra pure water. This allowed a comparison of the two different methods. A mean recovery rate for the aerosol collector of 92.7 ± 3.9 % was found for seven samples with an average concentration of 1.7 \(\mu\text{g m}^{-3}\) \(\text{SO}_4^{2-}\) measured with the filter method. The slightly lower yield of the aerosol collector can be explained with the instability of the particle generation which was monitored by an OPC during sampling.

**Field measurements at Dübendorf**

A first measurement campaign with the WEDD/AC technique was performed at Dübendorf during spring 1997. An overview of measured hourly mean concentrations of particulate nitrate and sulfate as well as of nitrous and nitric acid is given in Fig. 2.4. More detailed data measured at Dübendorf during April 1997 appear in Fig. 2.5 (HONO, \(\text{NO}_2\), CO and BC). As demonstrated above, the uptake of strong acids like HNO\(_3\) lower the pH of the effluent solution, and breakthrough of HONO can be observed accordingly, depending on the acidity of the sampled air. Assuming that particulate nitrite is only a minor fraction of the total nitrite under the prevailing acidic conditions, the ratio of HONO collected by the denuder to aerosol collector nitrite, which was between 0.07 and 10.58 with an average of 1.68, directly reflects this breakthrough. According to eq. (2) to (4) this corresponds to a pH range of < 3 to 5.6 with an average pH of 4.35 of the denuder effluent. The HONO data shown below always represent total nitrite from the denuder and the aerosol collector and are corrected for the \(\text{NO}_2\) interference (0.6%) of the aerosol collector.
Fig 2.4: Hourly mean concentrations of particulate nitrate and sulfate and gaseous HONO and HNO₃ measured at Dübendorf during March and April 1997. The time axis shows local standard time (LST).

During the whole observation period only small amounts of nitric acid were detected. Particulate nitrate often dominated over nitric acid, with an average HNO₃/total NO₃⁻ ratio of 0.04 (March data) and 0.17 (April data) respectively. Observed HONO levels of up to 3.2 ppb compare well with findings in other urban and suburban areas [Lammel and Cape, 1996, and references therein]. The data show the typical diurnal pattern with maxima in the early morning and minima typically during the afternoon mainly due to the efficient photolysis by sunlight. The average HONO/NO₂ ratio was 0.030 (day and night) and 0.044 (night only) during March and April 97, whereas the HONO/NOₓ ratio was 0.018 (day and night) and 0.024 (night only) respectively. This clearly points to additional formation of HONO in the atmosphere, because the average amount of HONO emitted from combustion sources is below 1% of NOₓ [ Andrés-Hernadez et al., 1996]. For
example, Kirchstetter et al. [1996] found an average HONO/NO\textsubscript{x} ratio of 0.0029 in a road tunnel.

Fig. 2.5: HONO (as total nitrite of the denuder and aerosol collector), NO\textsubscript{2}, BC and CO data measured at Dübendorf during April 1997. All data represent hourly mean concentrations.

Figure 2.6 displays the mean diurnal variation of the HONO to NO\textsubscript{2} ratio during April 1997, clearly showing the increase of this ratio during the night. Apparently, the decrease begins relatively late in the morning compared to sunrise. The BC and NO\textsubscript{x} data, also shown in Figure 2.6, mark the early morning emission peak. Thus, a strong source of HONO must be at work.
during the morning, the photolysis rate of HONO in full sun being on the order of $10^{-3}$ s$^{-1}$ [Bongartz et al., 1991]. The HONO forming process appears to persist also during the day, since otherwise the HONO to NO$_2$ ratio should drop well below 1% at noon.

![Graph showing diurnal variation of NO$_2$, NO$_X$, BC, HONO, and HONO/NO$_2$ ratio during the April campaign.](image)

Fig. 2.6: Daily medians showing the diurnal variation of NO$_2$, NO$_X$, BC, HONO and the HONO/NO$_2$ ratio during the April campaign.

None of the known gas phase mechanisms producing HONO is able to explain the HONO levels observed in the field [Lammel and Cape, 1996, and references therein], and heterogeneous HONO formation on any surface (ground and airborne) is currently being assumed. The disproportionation reaction with surface water (2.1), as the most likely reaction, is discussed:

$$2 \text{NO}_2 + \{\text{H}_2\text{O}\} \rightarrow \text{HONO} + \text{HNO}_3 \quad (2.1)$$

where $\{\text{H}_2\text{O}\}$ denotes water adsorbed on the surface. A reaction involving NO has been excluded by correlations found in recent field studies [Andrés-Hernandez et al., 1996, Harrison and Kitto, 1994, Harris et al., 1982]. This is
also confirmed by our measurements, where high HONO concentrations of more than 1.5 ppbv were observed in the complete absence of NO (data not shown).

Reaction (2.1) was studied in a number of laboratory studies [Salamaki et al., 1983, Svensson et al., 1987, Febo and Perrino, 1991]. However, these studies were performed under high NO\textsubscript{2} concentrations in the ppm region on materials of limited importance to the atmosphere. Recent studies have provided some evidence that at relevant NO\textsubscript{2} concentrations, NO\textsubscript{2} may be efficiently reduced to HONO on carbonaceous aerosol particles [Ammann et al., 1998] in the presence of water:

\[
\text{NO}_2 + \text{Red}_{\text{surface}} \rightarrow \text{NO}_2^- + \text{Ox}_{\text{surface}} \quad (2.2)
\]

The scatter plots and correlation coefficients of HONO versus NO\textsubscript{x}, NO\textsubscript{2} (precursor), CO and BC (as a potential surface for HONO formation) are shown in Fig. 2.7, both for the total data set and for the nighttime data between 22:00 and 05:00 local standard time. They exhibit a clear relationship with the highest correlation found between HONO and BC. The slopes of the correlation with NO\textsubscript{x}, CO and BC are lower during the day than during the night, due to photolysis of HONO. However, the HONO formation must be fast, enabling the build-up of significant HONO concentrations even during the daytime. The day-night difference is not found in the HONO-NO\textsubscript{2} plot, which is explained by the diurnal pattern of the NO\textsubscript{2} concentration. NO\textsubscript{2} on one hand shows a regular pattern related to local road traffic with maximum concentrations during the early morning and evening hours. On the other hand, NO\textsubscript{2} is adapting to the photostationary state (photolysis to NO, oxidation of NO by O\textsubscript{3}) during the day and eventually is produced from NO and O\textsubscript{3} during the night.
The results of the Dübendorf campaign are consistent with the heterogeneous formation of HONO according to reaction (2.1) or (2.2) on particle surfaces. Although the good correlation between HONO and BC supports the importance of reaction (2.2), a distinction of the two reactions is not possible from the present data and further work has to be done to elucidate the mechanisms by which HONO is formed in the atmosphere.
2.4 Conclusions

A measurement method for the combined, continuous and *in situ* analysis of atmospheric concentrations of HONO, HNO₃, and particulate nitrate and sulfate has been successfully established. The performance of the WEDD has been shown to critically depend on Henry's law, which in turn is directly related to the concomitant uptake of strongly acidic gases. To stabilize the pH of the denuder effluent, NaHCO₃ is added, which significantly improves the collection efficiency for HONO. The results of a first field campaign showed that both HONO/NO₂ ratio and HONO concentrations are of the same order of magnitude as at other comparable sites. Their diurnal variation and their relation to BC and NOₓ data point to a fast process forming HONO in the atmosphere. The observations are consistent with recent laboratory findings postulating HONO formation on soot aerosol particles in polluted air masses.
2.5 References


3 Summertime NO\textsubscript{y} Speciation at the Jungfraujoch, 3580 m above sea level, Switzerland

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C. Zellweger\textsuperscript{1,2}, M. Ammann\textsuperscript{1}, B. Buchmann\textsuperscript{2}, P. Hofer\textsuperscript{2}, M. Lugauer\textsuperscript{1}, R. Rüttimann\textsuperscript{2}, N. Streit\textsuperscript{1}, E. Weingartner\textsuperscript{1}, and U. Baltensperger\textsuperscript{1}

\textsuperscript{1}Paul Scherrer Institute, CH-5232 Villigen PSI, Switzerland
\textsuperscript{2}EMPA, CH-8600 Dübendorf, Switzerland

Abstract

During summer 1997, speciated reactive nitrogen (NO, NO\textsubscript{2}, peroxyacetyl nitrate (PAN), HNO\textsubscript{3} and particulate nitrate) was measured in conjunction with total reactive nitrogen (NO\textsubscript{y}) at the high-alpine research station Jungfraujoch (JFJ), 3580 m asl. The individually measured NO\textsubscript{y} components averaged to 82 % on total NO\textsubscript{y}. PAN was the most abundant reactive nitrogen compound and composed on average 36 % of NO\textsubscript{y}, followed by NO\textsubscript{x} (22 %), particulate nitrate (17 %) and HNO\textsubscript{3} (7 %). The NO\textsubscript{y}/NO\textsubscript{y} ratio averaged 0.25, but significantly lower values (0.15-0.20) were observed in the presence of high NO\textsubscript{y} mixing ratios. A classification of the data by synoptic weather conditions indicated that thermally-driven vertical transport has a strong impact on the mixing ratios measured at the JFJ during summer. A strong diurnal cycle with maximum mixing ratios in the late afternoon was observed for convective
days with north-westerly advection at 500 hPa. In contrast, during a period of convective days with a wind speed below 7.5 m s\(^{-1}\) at 500 hPa, no obvious diurnal cycle was observed. Under these meteorological conditions the convective boundary layer (CBL) can be significantly higher over the Alps (i.e., around 4 km asl) than over the surrounding lowlands. Subsequent advection may finally result in the export of reactive nitrogen reservoir compounds to the free troposphere, and hence influence global atmospheric chemistry.

3.1 Introduction

Reactive nitrogen compounds play a central role in the chemistry of the troposphere. Oxides of nitrogen (NO\(_x\) = NO + NO\(_2\)) are critical in determining atmospheric oxidation rates by influencing the photochemical production of ozone, and consequently the hydroxyl radical concentration in the troposphere [e.g. Crutzen, 1974, 1979; Roberts, 1995]. Therefore, a detailed knowledge of the sources, the chemical processes and the removal of reactive nitrogen from the atmosphere is important for understanding the chemistry of the atmosphere. The emissions of reactive nitrogen occur primarily as NO. Reactive nitrogen, abbreviated NO\(_y\), is defined as the sum of NO\(_x\) and its atmospheric oxidation products, abbreviated NO\(_z\). NO\(_x\), peroxacetyl nitrate (PAN), nitric acid and particulate nitrate are considered to be the most abundant NO\(_y\) compounds in the troposphere, while their relative abundance varies systematically [Singh et al., 1992]: NO\(_x\) is most abundant close to sources; PAN tends to be most abundant in regionally polluted air masses where there is more active organic photochemistry; and inorganic nitrate is most abundant in the more remote areas of the troposphere. Exceptions to this general trend appear to exist at high altitudes and latitudes of the northern hemisphere, where PAN is often of highest abundance. Due to its strongly temperature dependent thermal decomposition [Atkinson et al., 1992], PAN can act as a significant reservoir for nitrogen oxides in the colder regions of the troposphere.

Measurements of total reactive nitrogen (NO\(_y\)), especially in conjunction with measurements of speciated reactive nitrogen, have proven to be valuable in
assessing the photochemical processes that have occurred in an air parcel [e.g., Fahey et al., 1986; Doddridge et al., 1991; Jaffe et al. 1991; Atlas et al. 1992; Parrish et al., 1993; Sandholm et al., 1992, 1994; Wang et al., 1996; Williams et al., 1997; Liang et al., 1998]. The atmospheric lifetime of NOx and consequently the NOy/NOy ratio is dependent on photochemical activity and altitude. Since emissions of NOy occur as NOx, the NOy/NOy ratio reflects the photochemical processing that has occurred in an air parcel. The NOy/NOy ratio accounts for dilution effects, but wet and dry deposition and decomposition processes can complicate interpretation in regions remote from NOx emissions.

A problem that often arises for NOy budget observations is the so-called "shortfall of measured NOy" [Roberts, 1995]. The shortfall occurs when an instrument designed to measure all reactive nitrogen species by catalytic conversion measures greater NOy values than the sum of individually measured NOx, PAN and inorganic nitrate [e.g., Thompson et al., 1997]. There are three interpretations of the NOy shortfall. First, interfering compounds may result in an over-estimate of total NOy. Second, the shortfall may be due to the presence of reactive nitrogen compounds which are present in significant quantities but which are not measured in a given data set. Third, loss processes in the inlet system, e.g. adsorption of HNO3 [Neuman et al., 1999], may also lead to an underestimation of NOy.

Over the past few years, research on the global effects of NOy has focused on the role of NOx in the production of ozone. However, field studies of NOy compounds are relatively sparse in number and have not covered the temporal or geographic range needed to understand global NOy chemistry. It is for example still uncertain how important the role of stable NOy compounds such as PAN is in transporting NOx to the free troposphere [Roberts, 1995; Liang et al., 1998]. The NOy chemistry of the free troposphere is often studied with aircraft measurements or high-altitude observatories. However, aircraft based studies usually cover only a short temporal range, whereas longer time periods can be observed from mountainous measurement sites. Data from the latter have to be carefully evaluated in terms of convective boundary layer (CBL) influences caused by e.g. thermally-induced vertical transport processes or local wind systems.
This study presents results of ongoing NO\textsubscript{y} speciation including NO, NO\textsubscript{2}, PAN, HNO\textsubscript{3} and particulate nitrate measured during summer 1997 at the high-alpine site Jungfraujoch (JFJ) (46°33'N, 7°59'E), 3580 m asl, Switzerland, with respect to different meteorological situations.

### 3.2 Experimental

#### Measurement site

The JFJ station is located in the Sphinx observatory at 3580 m asl on the main crest of the Bernese Alps, Switzerland, and has been described earlier by Baltensperger et al. [1997]. The JFJ is incorporated in the Swiss National Air Pollution Monitoring Network (NABEL), which is maintained by EMPA Dübendorf on behalf of the Swiss Agency for the Environment, Forests and Landscape (BUWAL). NO, NO\textsubscript{2}, O\textsubscript{3} and CO are measured routinely and are available with a time resolution of 30 min. All meteorological parameters are measured by the Swiss Meteorological Institute (SMI). Furthermore, the JFJ high-alpine station has been the site of an aerosol program since 1988 [Baltensperger et al., 1997; Lugauer et al., 1998; Nyeki et al., 1998]. Due to the importance of monitoring long-term trends of gaseous and aerosol parameters in the free troposphere, the JFJ station has been incorporated into the Global Atmosphere Watch (GAW) program of the World Meteorological Organization (WMO). The JFJ is part of the combined European GAW virtual baseline station, additionally comprising the Zugspitze (2962 m, Germany) and Sonnblick (3106 m, Austria) high-alpine stations. A field campaign of reactive nitrogen compounds (NO\textsubscript{x}, HNO\textsubscript{3}, particulate nitrate, PAN, NO\textsubscript{y}) started on 18 July and ended on 23 August 1997.

#### Inlet system

Two inlet systems, both located on top of the Sphinx building, were used for NO\textsubscript{y} speciation. Except for HNO\textsubscript{3} and all particulate species, the NABEL station inlet was used. This inlet is made of stainless steel with an inside diameter (i.d.) of 8 cm and a total length of 3.1 m. The air flow rate through the steel part was 50 m\textsuperscript{3} h\textsuperscript{-1}. A heating system provided a constant gas flow.
temperature of 12°C. NOx, NOy and PAN instruments were connected directly to the inlet with PTFE tubing. Tubing extended to the center of the flow stream and was kept short (<1 m) in order to avoid sample losses. HNO3 and particulate nitrate were measured using the GAW aerosol inlet [Weingartner et al., 1999]. In addition to the original inlet system, a polyethylene tube of 3 m length (i.d. 4 mm) was used inside the heated stainless steel tube. The sample flow rate was 4 l min⁻¹.

**NOy measurement**

NO, NOx and NOy were measured with a commercially available instrument (Cranox, Ecophysics) using two chemiluminescence detectors (CLD 770 AL ppt) with temperature-controlled reaction chambers. In contrast to the standard Cranox instrument, the pressure in the NOx and NOy converters was regulated to 600 hPa. NOx was measured as NO after photolytic conversion (PLC 760). Compared to NOx reduction on a heated molybdenum surface, the photolytic conversion shows negligible interference of HNO3 and NH3 (each contributing less than 0.1% to NO2), PAN (<1-5%, depending on temperature) and HONO (< 20%) (according to the manufacturer). A detailed overview of possibly interfering compounds can be found in Feigl [1998]. NOy species were converted on a heated gold catalyst (300°C) with 2% CO (99.997%, Messer-Griesheim GmbH) as a reducing agent [Bollinger et al., 1983; Fahey et al., 1985, 1986]. This method has been shown to convert NOy species to nitric oxide with high efficiency (PAN, HNO3 ~94%, NO2; N2O5 ~98%, using 0.3% CO at 300°C, Fahey et al., 1985). Conversion efficiencies have been shown to be independent of the CO mixing ratio for CO additions between 0.1 and 5% [Feigl, 1998]. The instrumental detection limit for NO, NO2 and NOy was 50 ppt for 2 min and 20 ppt for 30 min average values, respectively.

**Measurement cycle and calibration**

NO and NOx were measured simultaneously using two separate CLDs. A CLD measurement cycle lasted 1 minute and included detection of the background chemiluminescence using a pre-reaction chamber for 30 s, followed by measurement of the total chemiluminescence in the main chamber for another 30 s. After the detection of NO and NOx, NOy was
analyzed using the same CLD as for NO. An automatic calibration of the instrument was performed every 24 hours. The chemiluminescence detectors were calibrated with NO standard (5 ± 0.1 ppm, diluted with zero air to 30 ppb) and zero air (dew point -20°C), and the conversion efficiencies of both converters were measured for NO2 by gas phase titration of NO with ozone. The NO, NO2 and NOy impurity of the zero air was checked daily. The NO standard mixture (NO 99.8% in N2 99.999%, Messer-Griesheim GmbH) was traced back to the National Institute of Standards and Technology (NIST) Reference Material. Agreement was within 2%. The conversion efficiency of the Au catalyst remained constant (95.7 to 98.7%) throughout the field campaign, and no cleaning was necessary during the experiment. Conversion efficiencies of the PLC ranged from 58.8 to 80.1%. The sensitivity of the NO/NOy detector was stable throughout the experiment with 0.356 ± 0.006 (standard deviation, 1σ) counts per second per parts per trillion (cps/ppt). The sensitivity of the NOx detector was 0.466 ± 0.021 (1σ) cps/ppt before 5 August and 0.351 ± 0.007 (1σ) cps/ppt from 6 August 1997. Based on photon counting statistics during the daily calibration the precision for levels well above the detection limit was ±2%, ±5%, and ±2% for NO, NO2 and NOy, respectively (1σ). Overall uncertainties in the measurements were estimated to be ±5% for NO, ±10% for NO2 and ±9% for NOy at ambient levels of 500 ppt (1σ). They include the precision of the CLDs, the NO standard uncertainty, the conversion efficiencies of the PLC (after linear detrending) and the Au catalyst, and artifact uncertainties of the zero air check.

The EMPA NOx and NOy measurements were compared at the JFJ during spring 1998 with measurements of the School of Environmental Sciences, University of East Anglia (UEA), Norwich (U.K.), to assess the overall measurement uncertainty. The inlet of the UEA custom-built system consisted of a ¼ inch PFA tube of 0.2 m length. Further details of the UEA instrument are given in Bauguitte [1998]. Agreement of the two systems was within 10% [L. Carpenter, personal communication, 1999].

**PAN measurement**

PAN was measured with a commercially available gas chromatograph (GC) and a calibration unit (Meteorologie Consult GmbH). The analytical method
was based on chromatographic separation with subsequent electron capture detection (ECD). Chromatographic separation (sample loop 2 ml) was performed every 10 minutes isothermally on a capillary column (Restek MTX-1, 0.53 mm diameter, 1 µm film) at 12°C. In contrast to the standard packed columns, the cooled capillary column showed a negligible PAN loss rate during contact with the stationary phase. A back-flushed pre-column prevented column contamination and reduced analysis run time by preventing substances with long retention times from entering the main column. No coeluting species were observed after thermal decomposition of PAN at 120°C in the inlet (according to the manufacturer). For the weekly calibration of the GC, PAN was generated by the photolysis of excess acetone and NO in zero air. NO was used as the concentration-determining compound. This allowed PAN measurements to be directly linked to the NO standard (10 ± 0.2 ppm NO 99.8% in N₂ 99.999%, Messer-Griesheim GmbH, traced back to NIST Reference Material) in the gas phase. The detection limit was 50 ppt. The overall measurement uncertainty was estimated to be ±3% (1σ), and included the uncertainty of the calibration standard, the NO and zero air flow during the calibration, and the integration precision of the GC.

**HNO₃ and particulate nitrate measurement**

HNO₃ and particulate nitrate measurements were carried out with the wet effluent diffusion denuder/aerosol collector (WEDD/AC) technique described in Chapter 2. This system enables diffusion-based gas collection with discrimination of gaseous analytes from their particulate counterparts. The aerosol particles were sampled after removal of the gases by means of steam condensation. Both denuder and aerosol collector solutions were preconcentrated on ion-exchange columns and analyzed by ion chromatography (IC), enabling a quasi-continuous measurement with an overall time resolution of 20 minutes. The detection limit was 10 ppt for HNO₃ and particulate nitrate. The overall uncertainty of the method was estimated to be ±19% (1σ), and included the uncertainties of the calibration standard, the integration precision of the IC, mass flowmeter calibrations, and the collection efficiencies of the denuder and aerosol collector.

In addition, weekly filter samples were taken during the field campaign. The
filter holders were attached to the handrail of the Sphinx roof, directly sampling ambient air. Double filter pack holders (polycarbonate, 47 mm diameter) were used to determine both particulate and gas-phase species. A teflon membrane filter (Sartorius SM11803, 1.2 μm pore size) was used for particulate nitrate, followed by a nylon membrane filter for HNO₃ (Gelman Nylasorb 66509, 1 μm pore size). Before use, the nylon filters were washed in 1 mM NaOH four times within 24 hrs to remove impurities. The filter packs were exposed to a flow rate of 1.5 l min⁻¹ for one week. Nylon filters were then extracted in 7 ml of 1 mM NaOH for 15 minutes in an ultrasonic bath and teflon filters in water only. A sample of 100 μl was injected directly into an ion chromatograph (DX-500, Microbore, column: AS-11, suppressor: ASRS-I, Dionex) with NaOH gradient elution and conductivity detection.

Particle measurements
The aerosol surface area concentration was measured using an epiphaniometer [Gäggeler et al., 1989]. This instrument detects the Fuchs surface area concentration which represents the total particle surface area accessible to a diffusing molecule [Pandis et al., 1991]. The data is corrected for the decline of the actinium source (T₁/₂ = 21.7 yrs) and was inverted using the algorithm presented in Rogak et al. [1991]. The raw data (units: counts per second, cps) were converted into a surface area concentration (μm² cm⁻³) by assuming a constant shape of the aerosol size distribution [Baltensperger et al., 1997]. The black carbon mass concentration was measured using an AE 10 aethalometer (Magee Scientific). This instrument measures the change of the attenuation (ATN) of visible light through a quartz fiber filter. The black carbon mass concentration per filter area, S_BC and the ATN are related by the linear relationship S_BC = ATN α⁻¹, where α is the mean instrumental absorption efficiency. From the attenuation, the black carbon concentration was determined using α = 9.3 m² g⁻¹ as determined by Lavanchy et al. [1999].

CO and O₃
Both CO and O₃ were continuously monitored by the NABEL network. Carbon
monoxide was measured using ND-IR technique with a commercially available instrument (APMA-360, Horiba). Calibration of the instrument was performed twice a month using CO calibration gas (8.25 ± 0.17 ppm CO 99.997% in N₂ 99.9995%, Messer-Griesheim, compared to NIST standard). An instrument zero check was performed daily using zero air (CO/CO₂ converter, molecular sieve 3 Å, Sofnocat). The zero drift was <2 ppb per day, and the detection limit was 30 ppb. The overall measurement uncertainty was estimated to be ±5% (1σ), and included the uncertainty of the calibration standard, the H₂O interference, and the instrument precision.

Ozone was measured using a commercially available monitor (Thermo Environmental Instruments, Model 49C, UV absorption). The instrument was compared to a transfer standard (TEI 49C PS) which was traced back to a NIST standard reference photometer. The detection limit was 0.5 ppb. The measurement uncertainty was determined to be ±2% (1σ), neglecting the uncertainty of the absorption coefficient.

### 3.3 Results and Discussion

**Meteorological conditions**

Meteorological conditions during the field campaign are characterized in Table 3.1 in terms of diurnal average values of temperature, wind speed and prevailing wind direction at the JFJ. In addition, Table 3.1 includes parameters characterizing the synoptic weather conditions over the central Alps for the individual days [Schüepp, 1979; Wanner et al., 1998]. In the following, the synoptic weather classification is abbreviated as SYNALP (SYNNoptic weather types of the ALPs). The key parameters of SYNALP are the surface pressure gradient and the height and slope of the 500 hPa pressure surface above the central Alps. The SYNALP classification defines 40 weather situations in total, which are grouped into 2 basic weather types. Vertical motion is dominant within convective weather types (surface pressure gradient < 5/444 hPa km⁻¹), and horizontal motion within advective types (≥ 5/444 hPa km⁻¹).
Table 3.1: Average temperature, wind speed and wind direction (local and at 500 hPa) at the Jungfraujoch during the field campaign, including basic (ADV = Adveective, CON = Convective, MIX = Mixed) and extended (prevailing wind direction for advective types, I = Indifferent conditions, A = Anticyclonic conditions) SYNALP weather types for the period between 18 July and 23 August 1997. Wind direction * refers to days when no wind direction prevailed. Symbols x and # denote special case studies described below.

<table>
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<tr>
<th>Date 1997</th>
<th>average temperature [°C]</th>
<th>average local wind speed [m s⁻¹]</th>
<th>wind direction at the Jungfraujoch</th>
<th>SYNALP basic weather type</th>
<th>SYNALP extended weather type</th>
<th>wind speed at 500 hPa [m s⁻¹]</th>
<th>wind direction at 500 h Pa</th>
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</tr>
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<td>A</td>
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<td>&lt; 7.5</td>
<td>*</td>
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<td>NW CON</td>
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<td>I</td>
<td>&lt; 7.5</td>
<td>*</td>
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<tr>
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<td>-0.8</td>
<td>4</td>
<td>* CON</td>
<td>I</td>
<td>&lt; 7.5</td>
<td>*</td>
<td></td>
</tr>
<tr>
<td>21 Aug</td>
<td>-0.9</td>
<td>4</td>
<td>NW CON</td>
<td>I</td>
<td>&lt; 7.5</td>
<td>*</td>
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</tr>
<tr>
<td>22 Aug</td>
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<td>3</td>
<td>NW CON</td>
<td>I</td>
<td>&lt; 7.5</td>
<td>*</td>
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</tr>
<tr>
<td>23 Aug</td>
<td>1.4</td>
<td>4</td>
<td>NW CON</td>
<td>A</td>
<td>&lt; 7.5</td>
<td>*</td>
<td></td>
</tr>
</tbody>
</table>

Within the convective weather types (denoted as CON in Table 3.1), 3 extended types are distinguished on the basis of the 500 hPa geopotential height. Synoptic scale vertical motion may be subsidence, associated with anticyclonic conditions (A), or lifting, associated with cyclonic conditions (C). Convective types without significant synoptic scale vertical motion are classified as indifferent conditions (I), i.e. flat pressure distribution. Within the advective (ADV) types, 4 extended weather types (W, N, E and S) are distinguished, according to the wind direction at the 500 hPa level. The mixed (MIX) weather type (Table 3.1, 1 August 1997) accounts for meteorological conditions when both convective and advective motions contribute significantly to atmospheric transport. On 1 August, cyclonic lifting prevailed.
at low elevations while a north-westerly jet at 500 hPa (wind speed: 30-35 m s\(^{-1}\)) caused strong advection.

According to the SYNALP classification, most of the measurement period was characterized by convective weather types with anticyclonic (A) or indifferent (I) conditions over the Alps. Daily maximum and minimum temperatures reached an average value of +2.1°C and -1.4°C respectively. Relative humidity was typically high, averaging 80% during the day and close to 100% during the night. Wind speed averaged around 5.4 m s\(^{-1}\), with no diurnal variation.

During the field campaign, a significant variability was observed for most of the parameters measured. One possible reason is that changes in the meteorological conditions cause the JFJ station to be influenced by different air masses. A question that arises regarding both diurnal and day-to-day variations is whether the air measured at the JFJ represents free tropospheric (FT) or convective boundary layer (CBL) influenced conditions. It can be seen that convective weather types were dominant during the measurement period. Exceptions occurred between 18 and 20 July when the advective weather type was observed, and on 1 August with a mixed weather type. The advective period between 18 and 20 July caused an increase in the mixing ratios of NO\(_x\) and NO\(_z\) (mainly PAN) and the NO\(_y\)/NO\(_y\) ratio. In contrast, particle concentrations (particulate nitrate, aerosol surface area concentration, BC) decreased and reached the lowest values during 19 July, which is explained by precipitation. The following period between 21 July and 31 July was characterized by convective conditions with an extensive anticyclone, i.e. flat pressure distribution (21-26, 29 and 31 July) or anticyclonic conditions over the Alps (27-28 and 30 July). During this period, several cyclones (e.g. 23 and 31 July) caused concentration changes in all measured species. Another cyclone passed the JFJ on 1 August resulting in a sharp concentration drop in all measured species except NO\(_x\). The following period between 3 and 23 August was characterized by very stable convective weather conditions over the Alps accompanied by an increase of the measured NO\(_z\) species. During this period, concentration drops are likely to be caused by local precipitation events or thunder storms.
**NO**\textsubscript{y} speciation

Figure 3.1 shows the time series of the mixing ratios of NO\textsubscript{x}, HNO\textsubscript{3}, particulate nitrate, PAN, NO\textsubscript{2}, as well as the NO\textsubscript{y}/NO\textsubscript{x} ratio. The sum of the measured individual NO\textsubscript{2} species is also given in Figure 3.1. Table 3.2 summarizes the mixing ratios of compounds measured at the JFJ during the summer campaign along with meteorological parameters. Figure 3.2 shows an overview of daily average mixing ratios of speciated and total NO\textsubscript{y} between 18 July and 23 August.

Table 3.2: Mean, median, standard deviation, minimum and maximum values of measured parameters during the summer field campaign (18 July to 23 August 1997) at the Jungfraujoch. All data are calculated from one-hour average values.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Mean</th>
<th>Median</th>
<th>Std. Deviation</th>
<th>Minimum</th>
<th>Maximum</th>
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<tr>
<td>NO ppt</td>
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<td>12</td>
<td>63</td>
<td>&lt;20</td>
<td>958</td>
</tr>
<tr>
<td>NO\textsubscript{2} [ppt]</td>
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<td>170</td>
<td>106</td>
<td>&lt;20</td>
<td>1131</td>
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<tr>
<td>NO\textsubscript{x} [ppt]</td>
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<tr>
<td>PAN [ppt]</td>
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<td>194</td>
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<td>853</td>
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<td>HNO\textsubscript{3} [ppt]</td>
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</tr>
<tr>
<td>Nitrate [ppt]</td>
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<td>148</td>
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<td>NO\textsubscript{x}/NO\textsubscript{y}</td>
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<td>9</td>
<td>22</td>
<td>75</td>
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<tr>
<td>CO [ppb]</td>
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<td>113</td>
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Aerosol surface area

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<th>Std. Deviation</th>
<th>Minimum</th>
<th>Maximum</th>
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<td>21</td>
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<td>277</td>
<td>236</td>
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<td>1323</td>
</tr>
<tr>
<td>Humidity [%]</td>
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<td>88</td>
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<td>100</td>
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<tr>
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<td>2.6</td>
<td>-7.7</td>
<td>7.5</td>
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</table>

Global radiation [W m\textsuperscript{-2}]
during daylight

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<th>Std. Deviation</th>
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<th>Maximum</th>
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<td>400</td>
<td>331</td>
<td>321</td>
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<td>1054</td>
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Wind Speed [m s\textsuperscript{-1}]

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<th>Std. Deviation</th>
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<td>[m s\textsuperscript{-1}]</td>
<td>5.4</td>
<td>5.1</td>
<td>2.2</td>
<td>1.6</td>
<td>14.9</td>
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Fig. 3.1: Time series of NO$_x$, PAN, HNO$_3$, particulate nitrate, NO$_2$ and NO$_x$/NO$_y$ during the field campaign at the Jungfraujoch. All data represent hourly mean values. The sum of individual NO$_2$ species is also given in the NO$_2$ diagram.
The sum of NO\(_x\), HNO\(_3\), particulate nitrate and PAN contributed on average 82% to the total NO\(_y\) mixing ratio. The major fraction of the total NO\(_y\) mixing ratio consisted of PAN (36%), followed by NO\(_x\) (19% NO\(_2\) and 3% NO), particulate nitrate (17%) and HNO\(_3\) (7%). The unidentified fraction (18%) is considered to consist of mainly peroxypropionyl nitrate (PPN), other organic nitrates and HNO\(_3\) losses (see below). However, it should be emphasized that an accurate determination of the NO\(_y\) shortfall is difficult due to the measurement uncertainties, as specified in section 3.2.

The relatively high PAN/NO\(_y\) ratio of 0.36 is in good agreement with other measurements at high altitudes over continental areas, where PAN was up to 77% of NO\(_y\) [Ridley et al., 1990; Singh et al., 1994]. In contrast, lower PAN/NO\(_y\) ratios are observed above the marine boundary layer or the marine free troposphere up to 4 km [Singh et al., 1990]. The second largest fraction with a total contribution of 24% of total NO\(_y\) was inorganic nitrate (HNO\(_3\) and particulate nitrate). On average, nitric acid amounted to 32% of total inorganic nitrate. Particulate nitrate measured with the aerosol collector averaged 167 ppt during the field campaign. Comparable results were obtained by the weekly filter samples with an average value of 181 ppt. However, a comparison of total inorganic nitrate between the filter pack (334 ppt) and the
WEDD/AC (239 ppt) resulted in a shortfall of 95 ppt for the WEDD/AC, which may be explained by a potential loss of nitric acid in the inlet system. Thus, the nitric acid data have to be regarded as lower limits, representing on average 47% of the filter pack measurements. This underestimation of nitric acid might explain about half of the NO\textsubscript{y} shortfall (10% out of 18%) assuming that no loss of nitric acid occurs at the inlet system used for the NO\textsubscript{y} measurement. NO\textsubscript{x} was the third largest fraction of total NO\textsubscript{y} during the field campaign. Except for a few occasional events, NO\textsubscript{2} was the dominating NO\textsubscript{x} species. This clearly indicates the absence of pollution sources in the immediate vicinity of the measurement station. As expected, the NO/NO\textsubscript{2} ratio was mainly governed by global radiation. It is noteworthy that during the whole field campaign the NO\textsubscript{x} mixing ratio remained relatively constant, in contrast to total NO\textsubscript{y} (see Fig. 3.2). This also means that the decline in the NO\textsubscript{y}/NO\textsubscript{x} ratio was mainly due to an increase of NO\textsubscript{2} species.

**Diurnal variations and day to day changes**

The diurnal variation of a certain species is influenced by both chemical reactions and meteorological conditions. It is therefore often difficult to attribute concentration changes to either one of them. In addition, thermally-induced vertical transport is accompanied by mixing of CBL and FT influenced air masses. This dilution has been estimated to be about a factor 5 to 10 at the JFJ for convective days with NW advection by comparing aerosol data measured in the CBL over the Swiss Plateau by Hering et al. [1998] with the JFJ data [Lugauer, 1998]. Results from the ongoing aerosol measurement program since 1988 have allowed for a detailed knowledge of vertical transport processes governing the aerosol concentration at the JFJ. Strong diurnal variations with highest mixing ratios in the late afternoon are often observed during the summer months [Nyeki et al., 1998]. Lugauer et al. [1998] showed that the diurnal variation of the aerosol concentration at the JFJ is not only dependent on thermally-induced transport processes but also on the wind direction. Two periods with convective meteorological conditions but different wind direction at 500 hPa were observed at the JFJ during the field campaign. The first period between 27 and 30 July was characterized by stable anticyclonic conditions with clear skies at the JFJ (case 1). The
prevailing wind, both locally and at 500 hPa was from the north-west. During
the second period between 16 and 22 August (case 2), the pressure
distribution over the Alps was flat, but convective conditions with mainly blue
skies and very low wind speed both locally and at 500 hPa prevailed. For the
following discussion we will mainly focus on these two time periods.

Case 1 (27 to 30 July 1997)
The time-series for the period from 27 - 30 July of NO, NOₓ, NOᵧ, NOₓ/NOᵧ,
PAN, HNO₃, particulate nitrate, CO, O₃, aerosol surface area concentration
and BC are given in Figure 3.3.
A very distinct diurnal cycle was observed for particle concentrations as well
as for NOᵧ and PAN. The diurnal pattern of the aerosol surface area
concentration compares well with the summer data from a nine-year data set
for convective and anticyclonic days with wind direction from N-NW at
500 hPa over the Alps described by Lugauer et al [1998]. We therefore
consider this period to be representative of the above meteorological
conditions. During the morning hours (0300-0900 CET) the JFJ station was
decoupled from the CBL, and the air is considered to represent free
tropospheric conditions. The diurnal period 0300 - 0900 has also been
suggested by Nyeki et al. [1998] to represent the FT-influenced period at the
JFJ. Concentrations started to increase by thermally-driven transport around
noon and peaked in the late afternoon. Peak concentrations of particulate
matter and NOᵧ species increased from day-to-day and reached their highest
level on 30 July. This reflects the general increase of air pollutants on the
Swiss plateau (NW of the JFJ) with peak ozone mixing ratios steadily
increasing from 38 to 69 ppb at Payerne (46°48'N, 6°56'E, 489 m asl) during
the same time period. However, Fig. 3.3 also shows that the nighttime
minima of these species remained relatively constant throughout the period.
After sunset polluted air masses are replaced by fresh FT-influenced air
through advective transport (wind direction NW). This typical diurnal cycle
was observed for all measured aerosol parameters (particulate nitrate, BC,
aerosol surface area concentration) as well as gaseous pollutants such as
NOₓ, PAN and NOᵧ. Under these meteorological conditions the CBL can be
significantly higher over the Alps (i.e., around 4 km asl) than over the
Fig. 3.3: Time series from 27-30 July 1997 of particulate nitrate, NO, NO$_x$, NO$_y$, NO$_x$/NO$_y$, PAN, HNO$_3$, CO, O$_3$, aerosol surface area and BC.
surrounding lowlands. Usually, PAN mixing ratios in air masses that are characteristic of remote areas do not show diurnal profiles with afternoon maxima, but rather more episodic behavior where PAN levels are determined by the long-range history of the air mass [Roberts, 1995]. Thus, the afternoon maximum at the JFJ is governed by thermally-induced vertical transport rather than long-range transport processes or in-situ photochemical formation. It is interesting that the nitric acid mixing ratio at the JFJ remained relatively constant throughout the day. In contrast, particulate nitrate showed a very distinct diurnal change. This indicates that the formation of particulate nitrate during the summer months is favored over the Swiss plateau due to neutralization of HNO₃. Assuming that the above-mentioned artifact during the HNO₃ sampling is constant with time and correcting the HNO₃ mixing ratio for this loss, the HNO₃/total nitrate ratio is calculated to be 0.81 for FT conditions and 0.22 for CBL-influenced conditions during this time period. Even though these numbers would need to be corroborated with artifact-free measurements, they indicate a strong vertical gradient of this ratio. Particulate nitrate may thus contribute a significant fraction to total inorganic nitrate in an air mass recently influenced by the CBL. A factor of 3 difference in the HNO₃/NOₓ ratio was also observed at Mauna Loa (Hawaii) between upslope and FT conditions [Atlas et al., 1992]. Therefore, neutralization of HNO₃ and fractionation into the aerosol phase may partly explain the discrepancy that is often observed between modeled [e.g. Wang et al., 1998; Thakur et al., 1999] and measured HNO₃, since the models do not consider the fact that part of the inorganic nitrate may be present as particulate nitrate. The diurnal cycle of NO was mainly governed by solar radiation and the availability of NO₂. Nighttime NO decreased below the detection limit through reaction with ozone. Carbon monoxide did not show such a pronounced diurnal cycle as PAN or NOₓ. This can be explained by the longer atmospheric lifetime and consequently the less pronounced vertical concentration profile of CO. Ozone levels did not show an obvious diurnal cycle and the mean mixing ratio remained at ~45 ppb throughout the day. This can be explained by the fact that ozone vertical concentration profiles are not pronounced during the afternoon, when thermally-induced transport occurs. Afternoon ozone peak mixing ratios at Payerne (46°48'N, 6°56'E,
489 m asl) and Chaumont (47°03'N, 6°59'E, 1140 m asl) reached 38 to 74 ppb. Considering the above-mentioned dilution of CBL with FT-influenced air, no diurnal cycle is therefore expected from vertical transport processes. Table 3.3 summarizes the mixing ratios of NO₃ species, CO, ozone, aerosol surface area and BC for FT-influenced (0300-0900) and CBL-influenced (1500-2100) air from 27-30 July. Average FT-influenced NO₃ was 244 ± 68 ppt rising to 1057 ± 458 ppt under CBL-influence.

Table 3.3: Mixing ratios of NO₃ species, carbon monoxide, ozone, black carbon (BC) and aerosol surface area concentration (AS) for FT-influenced (0300-0900 CET) and CBL-influenced air (1500-2100 CET) between 27 and 30 July 1997.

<table>
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<tr>
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<td>77</td>
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<td>22</td>
<td>68</td>
<td>41</td>
<td>9</td>
<td>7</td>
<td>0.12</td>
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<td>74</td>
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<tr>
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<td>48</td>
<td>156 &lt; d.l.</td>
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<td>18</td>
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<td>0.66</td>
<td>12</td>
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<td>CBL-influenced 1500-2100 (CET)</td>
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<tr>
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<td>191</td>
<td>1057</td>
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<td>27</td>
<td>202</td>
<td>0.20</td>
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<td>302</td>
</tr>
<tr>
<td>σ</td>
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<td>14</td>
<td>18</td>
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<td>6</td>
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</tr>
<tr>
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<td>58</td>
<td>282</td>
<td>282</td>
<td>1804</td>
<td>581</td>
<td>40</td>
<td>610</td>
<td>0.38</td>
<td>46</td>
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</tr>
</tbody>
</table>

During upward transport of CBL air to the free troposphere, the dilution of CBL air with FT air has to be considered. The dilution factor DL can also be estimated with this data using equation (1)

\[
(DL - 1)\frac{NO_3(FT)}{NO_3(CBL)} = \frac{NO_3(JFJ)}{DL}
\]
where $NO_y(FT)$ is the NO$_y$ mixing ratio in the free troposphere, $NO_y(CBL)$ is the NO$_y$ mixing ratio in the CBL and $NO_y(JFJ)$ is the NO$_y$ mixing ratio at the JFJ during the CBL-influenced period. Hering et al. [1998] reported NO$_y$ mixing ratios between 4.3 and 5.8 ppb with a NO$_x$/NO$_y$ ratio of 0.3 in the CBL over the Swiss Plateau from 29-30 July 1993. This period was characterized by meteorological conditions similar to case 1, and the mean NO$_x$ mixing ratio measured at Chaumont averaged 2.76 ppb (case 1, this study) and 2.79 ppb (29-30 July 1993). Using NO$_y$ of 4.3 to 5.8 ppb as reported by Hering et al. [1998] results in a dilution factor $DL$ of 5-7 for the time period 1500-2100 according to Equation (1). The NO$_x$/NO$_y$ ratio averaged 0.36 under FT-conditions and reduced to 0.20 under CBL-influence. The low NO$_x$/NO$_y$ ratio during the afternoon NO$_y$ peak compares to the NO$_x$/NO$_y$ ratios of 0.23 to 0.45 in the CBL over the Swiss Plateau reported by Hering et al. [1998] and indicates that photochemically aged air masses are transported to the JFJ. This suggests that transport from the sources to the JFJ requires more than a few hours and is a multi-step process. In the first step, NO$_x$ from emission sources is mainly oxidized to PAN and inorganic nitrate while forming a residual layer of photochemically aged air over the Swiss plateau. In the second step, thermally-induced vertical transport over mountainous slopes causes afternoon peak concentrations at the JFJ. Since NO$_y$ mixing ratios measured in the CBL over the Swiss Plateau [Hering et al., 1998] are significantly higher than at the JFJ, the NO$_x$/NO$_y$ ratio at the JFJ will be determined by CBL-influenced air during vertical transport events even when dilution with FT air by a factor 5-10 is considered, which explains the low NO$_x$/NO$_y$ ratio during these time periods.

The observed FT-influenced NO$_y$ mixing ratio of 244 ppt at the JFJ was slightly higher than at Mauna Loa (203 ppt during the night, MLOPEX II, [Atlas and Ridley, 1996]), but lower than the NO$_y$ mixing ratio of 392 ppt during the OCTA intensive at the high-altitude observatory of Izaña (Tenerife) [Fischer et al., 1998]. The difference between the median FT and CBL-influenced NO$_y$ mixing ratios was more pronounced at the JFJ (factor 4.1) compared to Izaña (factor 1.3) and Mauna Loa (factor 1.2) where similar upslope winds occur during a diurnal cycle. The higher day-to-night difference at the JFJ indicates higher pollution levels over continental areas.
Case 2 (16 to 22 August 1997)

The time series for the period from 16-22 August of NO, NO₅, NOy, NOₓ/NOy, PAN, HNO₃, particulate nitrate, CO, O₃, aerosol surface area and BC are given in Figure 3.4. Despite the convective weather conditions during this period, no obvious diurnal cycle but persistently high concentrations were observed for most of the days. A similar phenomenon is described by Lugauer et al. [1998] for the aerosol surface area concentration at the JFJ during convective days with anticyclonic conditions over the Alps when the wind direction at 500 hPa is south to south-west. They suggested that convective transport at different locations in the mountainous area south of the JFJ during southerly advection can cause high aerosol concentrations during the evening and nighttime. For convective days with a flat pressure distribution with south to south-westerly advection over the Alps, Lugauer et al. [1998] found only little diurnal variation of the aerosol surface area concentration (71 days, summer data from 1988 to 1996). Table 3.4 summarizes the mixing ratios of NOy species, CO, ozone, aerosol surface area and BC for the 0300-0900 and 1500-2100 time periods.

Average NOy was 1323 ± 457 ppt for the early morning period and 1696 ± 553 ppt in the late afternoon. The average NOₓ/NOy ratio was 0.22 and 0.15, respectively. The HNO₃/total nitrate ratio averaged 0.19 with no diurnal variation, indicating that the JFJ was influenced by CBL air throughout the whole period. In comparison to case 1, the pressure distribution over the Alps was flat, and the wind speed at 500 hPa was low. Concentration changes during this period were episodic rather than governed by diurnal processes. Thermally-induced vertical transport lead to increased mixing ratios in all measured species, but horizontal advection does not seem to have been effective enough to replace CBL-influenced air by free tropospheric air during nighttime. As a consequence, concentrations increased through daily injection of CBL-influenced air, leading to an average ozone mixing ratio of 66.5 ppb (20 to 22 August), which is 10.6 ppb above the 10-year average value for August (1988 to 1998).
Fig. 3.4: Time series from 16-22 August 1997 of particulate nitrate, NO, NOx, NOy, NOx/NOy, PAN, HNO3, CO, O3, aerosol surface area and BC.
Table 3.4: Mixing ratios of NO\textsubscript{y} species, carbon monoxide, ozone, black carbon (BC) and aerosol surface area concentration (AS) for the periods 0300-0900 CET and 1500-2100 CET between 16 and 22 August 1997.

<table>
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<tr>
<th></th>
<th>O\textsubscript{3} [ppb]</th>
<th>CO [ppb]</th>
<th>NO\textsubscript{x} [ppb]</th>
<th>NO\textsubscript{2} [ppb]</th>
<th>NO\textsubscript{y} [ppb]</th>
<th>PAN [ppt]</th>
<th>NO\textsubscript{3} [ppt]</th>
<th>NO\textsubscript{y}/NO\textsubscript{x}</th>
<th>Nitrate [ppt]</th>
<th>AS [\mu m\textsuperscript{2} cm\textsuperscript{-2}]</th>
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<tr>
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<tr>
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<td>883</td>
<td>0.27</td>
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</table>

The elevated mixing ratios throughout the day suggest that a simple time window filter is not effective enough to distinguish between FT- and CBL-influenced conditions during the summer months. Hence, data from the JFJ and other alpine measurement stations have to be carefully evaluated in terms of regional influence caused by different meteorological situations. There is an effort within the GAW program of the WMO to develop more sophisticated filters for extracting data with extended spatial representativity from such data sets. The periods with elevated concentrations at the JFJ also provide data highly relevant to the free troposphere, since subsequent advection will finally result in the export of reactive nitrogen reservoir compounds to the FT, and hence influence global atmospheric chemistry. Thus, the JFJ and other mountainous measurement stations allow air parcels to be studied both in the free troposphere and in transition from the CBL to the free troposphere.
Trace gas correlations

The relationship of reactive nitrogen species with CO and O₃ can provide valuable information on sources, transport, photochemical transformation and removal processes involving these species. If elevated levels of O₃ and NO₂ are a result of photochemistry involving anthropogenic precursors, a positive correlation between ozone and NO₂ is expected. Such a relation has been observed at different places over the North American continent [e.g. Olszyna et al., 1994; Kleinman et al., 1994] as well as over the Swiss Plateau [Hering et al., 1998]. However, a simple correlation between O₃ and NO₂ is not obvious from the present study ($R^2 = 0.42$, all data). In contrast to NO₂, ozone does not have a distinct diurnal cycle at the JFJ station, and the variability of the ozone mixing ratio is small compared to the variability of NO₂. It is however noteworthy that low ozone mixing ratios of less than 40 ppb were always accompanied by low NO₂ (< 500 ppt) levels.

A significant positive linear relationship was observed at the JFJ between NOₓ and CO during the CBL-influenced period. Figure 3.5 shows scatter plots and correlation coefficients of observed hourly mean NOₓ versus CO and NO₂ versus O₃ for the case 1 and the case 2 periods. Since CO and NOₓ undergo different formation and deposition processes, a simple correlation between these two species would not be expected. Thus, transport of CBL-influenced air to the JFJ is probably responsible for the positive correlation between the two species during the CBL-influenced period ($R^2 = 0.71$, case 1). In contrast, no correlation between CO and NOₓ was observed for FT conditions. Wang et al. [1996] found that a linear correlation between NOₓ and CO does not exist at Sable Island, Nova Scotia. However, a significant positive correlation between NOₓ and CO is described by Cárdenas et al. [1998] for polluted air masses on the North Norfolk coast, U.K. During the period with an advective weather type (18-20 July 97), no correlation between NOₓ and CO was observed ($R^2 = 0.12$). This can be attributed to the short lifetime of NO₂ species, e.g. through wet deposition of particulate nitrate and HNO₃.
Fig. 3.5: Scatter plots and correlation coefficients of observed hourly mean NO$_y$ versus CO and NO$_z$ versus O$_3$ at the JFJ for case 1 (27-30 July 1997) and case 2 (16-22 August 1997).

The NO$_y$/CO ratio reflects, similar to the NO$_y$/NO$_y$ ratio, the aging process that has occurred in an air parcel. In contrast to the NO$_y$/NO$_y$ ratio, the NO$_y$/CO ratio accounts for both dilution and deposition effects. Close to anthropogenic sources, the NO$_y$/CO ratio averages $\sim 0.1$ [Jaeglé et al., 1998]. In the city center of Berne (46°57'N, 7°26'E), an average NO$_y$/CO ratio of 0.073 was measured during the case 1 period. Considering only data from 0600 to 0900 CET, when vehicle traffic was at its maximum, a NO$_y$/CO ratio of 0.104 was observed. The NO$_y$/CO ratio was 0.043 during the case 1 period at the Chaumont station (representative for CBL conditions), assuming a NO$_y$ mixing ratio of 5 ppb. The difference between Chaumont and Bern can be explained by a deposition loss of NO$_y$ species. At the JFJ, the NO$_y$/CO ratio was 0.003 for the FT period and 0.010 for the CBL-influenced period during case 1, the former being comparable to values of $\sim 0.005$ from the upper troposphere [Jaeglé et al., 1998]. Hence air masses at the JFJ during FT periods are photochemically well-processed, and deposition processes of NO$_y$ species lead to low NO$_y$/CO and relatively high NO$_y$/NO$_y$ ratios in the FT air. The influence of thermally-induced vertical transport on the NO$_y$/CO ratio however can still be seen during the afternoon. During case 2, the NO$_y$/CO ratio averaged 0.010 for the morning period and 0.013 for afternoon period, which again suggests the influence of CBL air throughout the whole day.
during this period. Therefore, the NO$_y$/CO ratio may be helpful to detect CBL-influenced periods at the JFJ.

### 3.4 Conclusions

Speciated and total NO$_y$ was measured at the Jungfraujoch (JFJ). It was shown that NO$_y$ mixing ratios strongly depend on the synoptic weather conditions. During convective days with north westerly advection, a pronounced diurnal cycle with afternoon peak mixing ratios for NO$_y$, PAN, particulate nitrate and other aerosol parameters was observed. These peak mixing ratios were accompanied by a low NO$_x$/NO$_y$ ratio. Taking into account the dilution of CBL with FT air during vertical transport processes, the air transported to the JFJ is photochemically well-aged. Particulate nitrate was found to contribute significantly to total inorganic nitrate during upward transport. During a period with convective meteorological conditions accompanied by low wind speed at 500 hPa, highly elevated NO$_y$ mixing ratios were observed, indicating the influence of regional sources even during the nighttime.

Nighttime results for northwesterly advection are considered to represent free tropospheric conditions and the NO$_y$ data are comparable to FT data from other mountainous measurement stations (Izaña, Mauna Loa). However, the day-to-night difference is more pronounced at the JFJ than at the other sites, indicating higher pollution levels over continental areas. The data from the summer intensive also gave strong evidence that a time window is not sufficient to distinguish between FT conditions and CBL-influenced air masses at the JFJ, and further efforts to investigate the spatial representativity of the data is necessary. However, CBL-influenced periods allow air parcels to be studied during their transition from the CBL to the free troposphere through advection, where they possibly affect more remote areas of the troposphere through long-range transport. In a forthcoming paper, we will try to estimate this export of reactive nitrogen compounds to the free troposphere during the course of a year.
3.5 References


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4 A Two-Year Record of Reactive Nitrogen (NO$_y$) at a High Alpine Site (Jungfraujoch, 3580 m asl, Switzerland)

Submitted to the Journal of Geophysical Research

C. Zellweger$^{1,2}$, J. Forrer$^1$, P. Hofer$^1$, S. Nyeki$^{2,3}$, B. Schwarzenbach$^1$, E. Weingartner$^2$, U. Baltensperger$^2$

$^1$EMPA, CH-8600 Dübendorf, Switzerland
$^2$Paul Scherrer Institute, CH-5232 Villigen PSI, Switzerland
$^3$Institute for Environmental Research, University of Essex, Colchester, England

Abstract

Continuous measurements of total reactive nitrogen (NO$_y$) along with seasonal field campaigns of speciated NO$_y$ (NO, NO$_2$, peroxyacetyl nitrate (PAN), HNO$_3$ and particulate nitrate) were performed over a two-year period at the high-alpine research station Jungfraujoch (JFJ), 3580 m asl. The NO$_y$ mixing ratio and partitioning was shown to strongly depend on meteorological conditions. Knowledge of these meteorological transport processes allowed discrimination between undisturbed (i.e. clean) and disturbed (i.e. influenced by regional pollution sources) free tropospheric (FT) conditions at the JFJ. Median NO$_y$ concentration during undisturbed FT periods reached 350 ppt.
(winter) to 581 ppt (spring). Föhn events, synoptical lifting (e.g. fronts) and thermally induced vertical transport resulted in mixing ratios up to 10 times higher at the JFJ compared to undisturbed FT conditions. Furthermore this meteorological variability of the NO$_y$ concentration and partitioning often dominated the seasonal variability. Therefore the use of meteorological filters at the JFJ (and other mountainous sites) is crucial for the interpretation of data from such measurement sites.

4.1 Introduction

Reactive nitrogen compounds play a central role in the chemistry of the troposphere. Oxides of nitrogen (NO$_x$ = NO + NO$_2$) are critical in determining atmospheric oxidation rates by influencing the photochemical production of ozone, and consequently, hydroxyl radical concentration in the troposphere [e.g. Crutzen, 1979; Roberts, 1995]. The emissions of reactive nitrogen occur primarily as NO, followed by fast oxidation to NO$_2$. Reactive nitrogen, abbreviated NO$_y$, is defined as the sum of NO$_x$ and its atmospheric oxidation products, abbreviated NO$_2$. NO$_x$, peroxyacetyl nitrate (PAN), nitric acid and particulate nitrate are considered to be the most abundant NO$_y$ compounds in the troposphere, while their relative abundance varies systematically. For instance, NO$_x$ is most abundant close to sources; PAN tends to be most abundant in regionally polluted air masses where there is more active organic photochemistry; and inorganic nitrate is most abundant in the more remote areas of the troposphere. However, there is significant uncertainty in the levels and speciation of NO$_y$ in the non-urban troposphere due to a lack of measurements [Carroll and Thompson, 1995].

In the present study, we use measurements of total and speciated NO$_y$ obtained at the high Alpine Research Station Jungfraujoch (JFJ), Switzerland, to investigate the levels of nitrogen oxides in the free troposphere over Central Europe. Ongoing measurements of NO$_y$ started in March 1997 at the JFJ and were accompanied by seasonal measurement campaigns of speciated NO$_y$. The JFJ is one of 16 measurement sites of the Swiss National Air Pollution Monitoring Network (NABEL). Furthermore, the JFJ high-alpine station has been the site of an aerosol program since 1988
Due to the importance of monitoring long-term trends of gaseous and aerosol parameters in the remote troposphere, the JFJ station has been incorporated into the Global Atmosphere Watch (GAW) program of the World Meteorological Organization (WMO). The JFJ is part of the combined European GAW virtual baseline station, additionally comprising the Zugspitze (2962 m, Germany) and Sonnblick (3106 m, Austria) high-alpine stations. Although air-quality monitoring networks provide observations of the spatial and temporal variation of trace gases, they usually provide no information on chemistry above ground and higher. Aircraft observations have shown that surface and upper air chemistry are frequently decoupled [Berkowitz et al., 1998]. As a consequence, surface measurements are in general only representative of measurements near the ground. In contrast, mountains are often decoupled from the planetary boundary layer and measurements are therefore representative of a larger region. At mountainous stations it is, however, crucial to develop methods to detect periods which are influenced by regional pollution sources. The main topic of this work was to investigate the influence of different meteorological processes on the NO$_x$ mixing ratio and speciation over the Alpine region. Measurements over a two-year period from April 1997 to March 1999 are presented.

Another important issue is the relevance of the Alpine region on mountain venting of convective boundary layer (CBL) airmasses into the free troposphere (FT). While the magnitude, distribution, and time dependency of aircraft NO$_x$ emissions to the FT are better quantified, the contribution of other sources, such as convective transport from the surface, and recycling of its oxidation products (such as HNO$_3$ and PAN) is much less certain [Lee et al., 1997]. Recent aircraft observations of large-scale NO$_x$ plumes [Brunner et al., 1998] downwind of convective areas, mainly located over the continents, suggest that vertical transport may be a significant source of NO$_x$ in the upper troposphere.
4.2 Experimental

Ongoing NO$_y$ measurements started in March 1997 at the JFJ. The measurement station and instrumentation have already been described in detail elsewhere (see below). Therefore, only a brief summary of experimental aspects is presented here.

Measurement site and inlet system

The high alpine research station Jungfraujoch (46°33'N, 7°59'E, 3580 m asl) is located on the main crest of the Bernese Alps, Switzerland [e.g., Baltensperger et al., 1997]. Two inlet systems, both located on top of the Sphinx building, were used for NO$_y$ speciation. A detailed description including the dimensions and flow rates can be found in Chapter 3.

Instrumentation

NO, NO$_x$, and NO$_y$ were measured with a commercially available instrument (Cranox, Ecophysic) using two chemiluminescence detectors (CLD 770 AL ppt) with temperature-controlled reaction chambers. NO$_x$ was measured as NO after photolytic conversion (PLC 760). NO$_y$ species were converted on a heated gold catalyst (300°C) with 2% CO (99.997%, Messer-Griesheim GmbH) as a reducing agent [Bollinger et al., 1983; Fahey et al., 1985, 1986]. A full description of the instrumentation including interferences, conversion efficiencies, statistics and sensitivities can be found in Chapter 3.2. An automatic calibration of the instrument was performed every 23 hours. The chemiluminescence detectors were calibrated with NO standard gas (5 ± 0.1 ppm, diluted with zero air to 30 ppb) and zero air (dew point -20°C), and the conversion efficiencies of both converters were measured for NO$_2$ by gas phase titration of NO with ozone. If the conversion efficiency dropped below 95% (~ every 3 months), the Au catalyst was cleaned with ethanol, acetone and ultrapure water. The conversion efficiencies of the PLC ranged from 45 to 82%. The NO, NO$_2$ and NO$_y$ impurity of the zero air was checked daily. The NO standard mixture (NO 99.8% in N$_2$ 99.999%, Messer-Griesheim GmbH) was traced back to the National Institute of Standards and
Reactive nitrogen at the Jungfraujoch

Technology (NIST) Reference Material. The instrumental detection limit for NO, NO\textsubscript{2} and NO\textsubscript{y} was 50 ppt for 2 min and 20 ppt for 30 min average values, respectively. Overall uncertainties in the measurements were estimated to be ±5% for NO, ±10% for NO\textsubscript{2} and ±9% for NO\textsubscript{y} at ambient levels of 500 ppt (1\sigma). They include the precision of the CLDs, the NO standard uncertainty, the conversion efficiencies of the PLC (after linear detrending) and the Au catalyst, and artifact uncertainties of the zero air check. Our NO\textsubscript{x} and NO\textsubscript{y} measurements were compared at the JFJ during spring 1998 with measurements of the School of Environmental Sciences, University of East Anglia (UEA), Norwich (U.K.), to assess the overall measurement uncertainty. The inlet of the UEA custom-built system consisted of a ¼ inch PFA tube of 0.2 m length. Further details of the UEA instrument are given in Bauguitte [1998]. Agreement of both systems was within 10% [Carpenter et al., 2000].

PAN was measured with a commercially available gas chromatograph (GC) and a calibration unit (Meteorologie Consult GmbH) coupled to an electron capture detection unit (ECD). The instrument and the calibration procedure is described in Chapter 3.2. The detection limit was 50 ppt, and the overall measurement uncertainty was estimated to be ±3% (1\sigma).

HNO\textsubscript{3} and particulate nitrate measurements were carried out with the wet effluent diffusion denuder/aerosol collector (WEDD/AC) technique described by Blatter et al. [1994] and Simon and Dasgupta [1995]. The detection limit was 10 ppt for HNO\textsubscript{3} and particulate nitrate. Details of the instrument are described in Chapter 2.2.

Both CO and O\textsubscript{3} were continuously monitored with commercially available instruments by the NABEL network (APMA-360, Horiba, for CO; Thermo Environmental Instruments, Model 49C, for O\textsubscript{3}). The detection limit was 30 ppb for CO and 0.5 ppb for O\textsubscript{3}. More detailed information including measurement uncertainties and the calibration procedure can be found in Chapter 3.2.

The aerosol surface area concentration was measured using an epiphanometer [Gäggeler et al., 1989]. This instrument detects the Fuchs surface area concentration which represents the total particle surface area accessible to a diffusing molecule [Pandis et al., 1991]. The data is corrected for the decline of the actinium source (T\textsubscript{1/2} = 21.7 yrs) and was inverted using
the algorithm presented in Rogak et al. [1991]. The raw data (units: counts per second, cps) were converted into a surface area concentration (μm² cm⁻³) by assuming a constant shape of the aerosol size distribution [Baltensperger et al., 1997]. This assumption has been shown to be valid for the accumulation mode, which dominates the surface area distribution at the JFJ [Weingartner et al., 1999]. The relative statistical error of the epiphanometer signal was found to be 7% for median winter concentrations and negligible for summer concentrations.

Definition of meteorological filters

Since the main emphasis of measurements at the JFJ was to examine the influence of meteorological transport processes on tropospheric chemistry over the Alpine region, care was taken to identify and separate periods with a potential perturbation due to local or regional pollution sources. The data was therefore divided into two periods, "undisturbed" and "disturbed" free tropospheric (FT). The term "disturbed FT" is used to account for the various processes involved during dilution of PBL air with FT air during upward transport. For instance, the contribution of PBL to undisturbed FT airmasses was estimated at 14 – 20% during convection events. This corresponds to a dilution factor of ~5 - 7 of PBL by FT airmasses (see Chapter 3.3). In this work, disturbed FT conditions are defined as FT airmasses that have been mixed with PBL airmasses due to any of the following meteorological conditions: 1) föhn (or chinook) events, 2) synoptical lifting (e.g. frontal systems), and 3) thermally induced vertical transport. These three conditions may significantly influence concentrations of gaseous and aerosol parameters.

Data were categorized in the priority 1)>2)>3) in order to optimize discrimination, and criteria are further described below.

1) Föhn events were excluded from the FT data using a procedure described by Forrer et al. [2000]. In addition to the work of Forrer et al. [2000], north (NF) and south föhn (SF) events were distinguished. The following criteria were used to detect föhn events, in which all criteria had to be fulfilled:
The absolute north-south pressure difference over the Alps using data from the Stabio (Southern Switzerland) and Schaffhausen (Northern Switzerland) meteorological stations was > 2.1 hPa / 100 km according to Hoinka [1980].

The relative humidity on the lee side of the Alps using data from Altdorf for south-fohn and Locarno-Monti for north-fohn events was < 50%, and accompanied by precipitation at the other station.

The local wind speed at the JFJ was > 10 m s\(^{-1}\).

These criteria were verified by comparison with weather charts, the Swiss Meteorological Institute (SMI) bulletin and 3-D back-trajectories.

2) Synoptical lifting (SYN) (e.g. frontal systems) was excluded from the undisturbed FT data by running 3-D back-trajectories calculated by the TRAJEK DWD-model [Fay et al., 1995] using the wind fields of the Swiss Model (SM). The SM is a hydrostatic numerical weather prediction model with a grid size of ~14 km, which is operationally used at the SMI. The arrival location of the calculated trajectories was the JFJ, and the altitude was set to 700 hPa in the model. The trajectories were then analyzed with respect to their minimum height (corresponding to maximum pressure) 24 hours previous to their arrival time. If the trajectory height dropped below the 850 hPa level for at least four hours, the data were excluded from the undisturbed FT data set. These criteria were verified by comparison with data from the Alpine Weather Statistics (AWS) scheme [Schüepp, 1979; Wanner et al., 1998; Forrer et al., 1999].

3) Periods where thermally induced vertical transport (THER) occurred were excluded from undisturbed FT data using the following procedure:

Periods with diurnal peak concentrations between February 15 and October 15 were excluded from FT conditions by comparing the mean concentrations of NO\(_y\) for the diurnal periods between 0300 to 0900 CET on two consecutive days with the period from 1500 to 2100 CET between the morning periods. If NO\(_y\) was =50% higher during the afternoon period,
only the data from 0300 to 0900 CET was considered to represent undisturbed FT conditions. If no NOy data was available, the aerosol surface area concentration was used because of its similar diurnal behavior during thermally induced vertical transport at the JFJ (see Chapter 3.3). If both NOy and aerosol surface area concentration data were missing, the specific humidity (q) was used. For q, the criterion for thermally induced vertical transport was a \( \pm 25\% \) higher concentration during the afternoon in comparison to the morning periods (same time intervals as above).

- Convective days (anticyclonic or indifferent conditions) from March to September with low wind speed at the 500 hPa level were excluded entirely from the FT data. Such periods were shown to be influenced by CBL air masses throughout the whole day (see Chapter 3.3).

**4.3 Results and Discussion**

**Seasonal variation and meteorological transport processes**

An overview of monthly median and mean NOy, NOx, NO, PAN, O3 mixing ratios and the NOy/NOy ratio since April 1997 is given in Figure 4.1 for the entire data set. Generally higher concentrations were observed during spring and summer, due to enhanced vertical transport processes during these seasons, and in the case of PAN higher production rates within the CBL. The monthly mean values of NO, NOx and NOy were often found to be a factor of two or more higher than the corresponding median values. This can be attributed to periods with transport of polluted air masses from source regions to the JFJ caused by various meteorological processes. Figure 4.2 shows the frequencies of the meteorological situations described in Chapter 4.2 for the winter and summer half-year of the period between April 1997 and March 1999. As expected, thermally induced vertical transport occurs predominately during spring and summer, whereas frontal systems and fön events occur all year round.
Fig. 4.1: Seasonal variation in monthly mean and median values of NO$_y$, NO$_x$, NO, PAN, O$_3$ and the NO$_x$/NO$_y$ ratio from April 1997 to March 1999. The first and third quartiles are indicated by bars. Only data where > 75% of the hourly values were available are shown.
Fig. 4.2: Frequencies of meteorological processes (NF, SF = north and south föhn, THER = thermally induced vertical transport, SYN = synoptical lifting) for the period between April 1997 and March 1999. Results shown for winter (September to February) and summer (March to August) half-year periods.

Table 4.1 gives an overview of seasonal median and mean NOx, NOy, PAN, HNO3, particulate nitrate, CO, O3 and the aerosol surface area concentration measured at the JFJ for the period from April 1997 to March 1999.

Table 4.1: Seasonal median and mean values of NOx, NOy, PAN, HNO3, particulate nitrate, CO, O3, and the aerosol surface area concentration with standard deviation (s.d.) and number of measurements (N) based on hourly values at the JFJ for the period from April 1997 to March 1999, for the whole data set, as well as for undisturbed and disturbed FT conditions.

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<th>Disturbed FT</th>
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<td>O3 [ppb]</td>
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### Table 4.1

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<td>CO [ppb]</td>
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**Summer**

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**Autumn**

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<tr>
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<td>105</td>
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<tr>
<td>HNO$_3$ [ppt]</td>
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<tr>
<td>NO$_3^-$ [ppt]</td>
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<tr>
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<td>AS [µm$^2$cm$^{-3}$]</td>
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<td>6</td>
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</table>

**Winter**

Table 4.1 includes the whole data set based on hourly values, undisturbed FT conditions, and disturbed FT conditions. It can be seen from Table 4.1
that the NO\textsubscript{y} mixing ratio is comparable during the spring and summer months (median NO\textsubscript{y} 766 ppt and 702 ppt, all data) and during the autumn and winter months (median NO\textsubscript{y} 495 ppt and 411 ppt, all data). This is also the case for the NO\textsubscript{x} and PAN mixing ratios, while the aerosol surface area concentration, particulate nitrate and nitric acid showed maximum concentrations during the summer months. The effect of data filtering for NO\textsubscript{x}, NO\textsubscript{y}, PAN and the aerosol surface area concentration is illustrated in Figure 4.3, where monthly median mixing ratios are shown for the filtered data set as well as for föhn events, synoptical lifting and thermally induced vertical transport.

It can be seen that the meteorological processes described in Chapter 4.2 caused an increase of the mixing ratios as well as of the variability for NO\textsubscript{x}, NO\textsubscript{y} and PAN. The effect was most pronounced for NO\textsubscript{x} as a primary pollutant with a strong vertical concentration gradient. Different behavior was observed for the aerosol surface area concentration, where higher values were observed only for thermally induced vertical transport. The lower values for the aerosol surface area concentration during föhn events and synoptical lifting can be explained by precipitation scavenging during these transport events. This mechanisms is the major sink for the aerosol area surface concentration. Thus, the summer maximum of aerosol parameters, particulate nitrate and HNO\textsubscript{3} can be explained by thermally induced vertical transport processes, where wet deposition is of minor importance.

Frequency distributions of NO\textsubscript{x}, NO\textsubscript{y}, the NO\textsubscript{x}/NO\textsubscript{y} ratio, PAN, the aerosol surface area concentration, and CO are shown in Figure 4.4. For each species, undisturbed FT conditions, north and south föhn events, synoptical lifting and thermally induced vertical transport data are shown separately. The plots in Figure 4.4 are based on hourly mean values, and for each species the data was divided into 50 bins.
Fig. 4.3: Monthly median values of NOx, NOy, PAN and the aerosol surface area concentration for the filtered data set as well as for different meteorological situations from April 1997 to March 1999. The first and third quartiles are indicated by bars.
Fig. 4.4: Frequency distributions including median, mean and number (N) of values for NOy, NOx, CO, PAN, O3, the aerosol surface area concentration (AS) and the NOy/NOx ratio from April 1997 to March 1999 for the whole data set and different meteorological situations. For each species, the data set was based on hourly values and divided into 50 bins.
Fig. 4.4: cont.
It can be seen from Figure 4.4 that the mixing ratios of NO$_x$, NO$_y$, CO, PAN and the NO$_x$/NO$_y$ ratio were elevated during south föhn events, in conjunction with low aerosol concentrations. Similar increases of the CO and NO$_x$ mixing ratios at the JFJ during south föhn episodes were also observed by Forrer et al. [1999] for the period between April 96 and November 97. During the observation period between April 97 and March 99, 4.1% of the data fulfilled the criteria for south föhn. Although these events are less frequent than thermally induced vertical transport or synoptical lifting, they may significantly add to the upward transport of gaseous species over the Alpine region. Forrer et al. [1999] showed by trajectory analysis that air masses reaching the JFJ during south föhn episodes from the south and southeast seem to be frequently below the 900 hPa level and are therefore likely to be influenced by sources from this region. The influence of source regions during south föhn events can also be seen from the present data set, where a median NO$_x$ mixing ratio of 0.5 ppb was observed during south föhn events, with 11% of the data being above 2.5 ppb. This is significantly higher compared to undisturbed FT values with a median NO$_x$ mixing ratio of 0.11 ppb. The NO$_x$/NO$_y$ ratio was also significantly higher during south föhn events compared to the undisturbed FT. In contrast, only a very low aerosol surface area concentration was observed, which can be explained by wet deposition. Similar behavior was observed for north føhn events, which occurred with a frequency of ~5% between April 1997 and March 1999. Figure 4.4 shows that the NO$_x$/NO$_y$ ratio was comparable to south føhn events, in conjunction with low aerosol surface area concentrations. However, the mixing ratios of gaseous species (NO$_x$, PAN, total NO$_y$) were lower compared to south føhn events. Explanations for this may be the different pollution levels north (Swiss plateau) and south (Po basin) of the Alps and the orographic situation.

Synoptical lifting (e.g., frontal systems) is another important transport process for NO$_y$ species, which may be enhanced by Alpine orography. It can be seen from Figure 4.4 that NO$_x$, NO$_y$, PAN and CO rich air was transported to the JFJ during synoptical lifting. The frequency distributions of these compounds during synoptical lifting are comparable to north føhn events. In contrast to føhn events, the aerosol surface area concentration increased slightly. This may be explained by better vertical mixing and less precipitation.
during synoptical lifting. Thermally induced vertical transport also leads to increased NO\textsubscript{y} and aerosol surface area concentrations (see Figure 4.4). Thermally induced vertical transport has been recognized as an important mechanism of upward transport to the JFJ for aerosol particles [Baltensperger et al., 1997; Lugauer et al., 1998; Nyeki et al., 1998], as well as for gaseous species (see Chapter 3.3).

The identification of thermally induced vertical transport was based on the diurnal variation of NO\textsubscript{y}, the aerosol area surface concentration, and the specific humidity (see Chapter 4.2). This is in contrast to earlier studies [Lugauer et al., 1998] where thermally induced transport was determined according to the Alpine Weather Statistics (AWS) scheme [Schüepp, 1979; Wanner et al., 1998]. Convective AWS days during spring and summer usually exhibit a pronounced diurnal cycle with afternoon peak concentrations for both aerosol and some gaseous parameters. However, a strong diurnal variation was also observed on several non-convective days according to the AWS classification (e.g. March 31, 1998, AWS Adveective type). This might be due to the fact that the AWS classification covers the whole Alpine region and does not account for local wind systems. Figure 4.5 illustrates diurnal variations of the median NO\textsubscript{y}, O\textsubscript{3}, and aerosol surface area concentration over the four seasons at the JFJ for days with thermally induced vertical transport and for the undisturbed FT. The aerosol surface area concentration and NO\textsubscript{y} showed a distinct diurnal cycle with afternoon maximum concentrations at ~1800 CET during days with thermally induced vertical transport. A detailed overview of diurnal cycles is given in Lugauer et al. [1998] and Nyeki et al. [1998] for aerosol parameters and in Chapter 3.3 for gaseous species. The diurnal cycle of radon daughters was described recently [Lugauer et al., 2000]. Ozone showed only a very weak diurnal variation for days with thermally induced vertical transport during spring, and no diurnal variation was observed for the rest of the year. This can be explained by small vertical concentration gradients in combination with dilution by FT air during convective transport.
Fig. 4.5: Diurnal variation of seasonal median values of gas and aerosol parameters from April 1997 to March 1999 at the Jungfraujoch Station. The four seasons are defined as summer, June to August, etc. The left panel shows days with thermally induced vertical transport, whereas undisturbed FT data is shown in the right panel. No winter data are shown for thermally induced vertical transport due to the small number of days with convection during winter.
Figure 4.4 shows that the lowest NOx/NOy ratios were observed during thermally induced upward transport at the JFJ. The NOx mixing ratios during these periods were comparable to values of the undisturbed FT, whereas a significant increase of the NOy mixing ratios was observed. Therefore, air masses reaching the JFJ through thermally induced vertical transport are photochemically well-processed. Aspects of mountain venting of CBL air into the FT through thermally induced vertical transport will be discussed further below.

Air mass aging

The fact that lower NOx/NOy ratios were observed during thermally induced upward transport compared to undisturbed FT conditions at the JFJ suggests that the NOx/NOy ratio is not always a suitable parameter to estimate the processing that has occurred in an air parcel. This is especially the case for remote locations, where deposition (e.g., wet and dry deposition of HNO3) and decomposition processes (e.g., thermal decay of PAN) can make the ratio difficult to interpret. The NOx/NOy ratio accounts for the photochemical processing that has occurred in an air parcel. The photochemical aging of an air parcel may be fast, with NOx/NOy ratios < 0.4 within a few hours. Thus, this ratio may be used to assess the photochemical processing close to sources and on a time scale of less than one day. An alternative parameter to assess the aging process that has occurred in an air parcel is the NOy/CO ratio, which accounts for both deposition and dilution effects. Close to anthropogenic sources, the NOx/CO ratio averages ~0.1, whereas values of ~0.005 are observed in the upper troposphere [Jaegle et al., 1998]. However, it should be noted that the NOy/CO ratio also shows a seasonal variation, with lower values during the winter months due to a longer lifetime of CO. Figure 4.6 shows seasonal plots of the NOx/NOy versus NOy/CO ratios for different meteorological situations and the undisturbed FT. It can be seen that undisturbed FT conditions are always accompanied by the lowest NOy/CO ratios, indicating advanced aging of these air masses. This ratio may therefore be an alternative method to distinguish between disturbed and undisturbed FT conditions at the JFJ.
Fig. 4.6: NO$_x$/NO$_y$ versus NO$_y$/CO ratios for south föhn (SF), thermally induced vertical transport (THER), synoptical lifting (SYN) and the undisturbed FT. Four seasons are shown (MAM = March to May, etc.). The first and third quartiles are indicated by bars.
NO$_y$ partitioning

Summertime NO$_y$ speciation at the JFJ has already been discussed in Chapter 3. The most abundant NO$_y$ species was PAN with an average contribution of 36%, followed by NO$_x$ with 22%, particulate nitrate with 17% and HNO$_3$ with 7%. The sum of NO$_x$, HNO$_3$, particulate nitrate and PAN contributed on average 82% to the total NO$_y$ mixing ratio. However, it should be emphasized that an accurate determination of total NO$_y$ with individually measured species is difficult due to measurement uncertainties. Furthermore, the presence of reactive nitrogen compounds which are present in significant quantities but which are not measured in a given data set may also lead to an underestimation of total NO$_y$.

Figures 4.7 and 4.8 show mixing ratios of individually measured NO$_y$ species as well as total NO$_y$, the NO$_y$/NO$_x$ and the NO$_y$/CO ratios and the aerosol surface area concentration measured at the JFJ during winter and spring 1998, respectively. The periods with occurrence of south föhn, synoptical lifting and thermally induced vertical transport are also shown in Figures 4.7 and 4.8 (no situation with north föhn occurred during these periods). It should be noted that the NO$_y$/CO ratio increased on average during the periods with occurrence of the above meteorological situations (see Figs. 4.7 and 4.8), in accordance with the conclusion drawn above. The NO$_y$ partitioning for selected periods is shown in Figure 4.9a-c. During the undisturbed FT period from February 12 - 13, 1998 (see Fig. 4.9a), NO$_x$ was with 46% the most abundant NO$_y$ species, followed by PAN (20%), HNO$_3$ (9%) and particulate nitrate (3%). An average fraction of 22% could not be identified, and total NO$_y$ averaged 209 ppt. This period can be considered as representative of clean conditions during the autumn and winter months, since total NO$_y$ remained almost constant throughout February 1998 with the exception of the periods when synoptical lifting and thermally induced vertical transport was observed. During periods influenced by synoptical lifting (February 22-23, 1998, 0700-1900, Fig. 4.9b), PAN was the most abundant NO$_y$ species (38%), followed by NO$_x$ (26%), HNO$_3$ (1%) and particulate nitrate (1%). The peak concentration of NO$_y$ was more than 10 times higher during this period compared to the "clean" period, and mainly PAN together with an unidentified fraction was transported to the JFJ. The very low contribution of inorganic
Fig. 4.7: Time series of hourly mean values of NO$_y$, HNO$_3$, NO$_3$, NO$_x$, PAN, aerosol surface area concentration, the NO$_x$/NO$_y$ and the NO$_y$/CO ratios together with the sum of the individually measured NO$_y$ species for February 1998. The occurrence of south föhn (SF), synoptical lifting (SYN) and thermally induced vertical transport (THER) is also shown.
Fig. 4.8: Time series of hourly mean values of NO$_x$, HNO$_3$, NO$_3^-$, NO$_x$, PAN, aerosol surface area concentration, the NO$_x$/NO$_y$ and the NO$_x$/CO ratios together with the sum of individually measured NO$_x$ species from 20 March to 16 April 1998. The occurrence of south fohn (SF), synoptical lifting (SYN) and thermally induced vertical transport (THER) is also shown.
Fig. 4.9: Average hourly mixing ratios of speciated and total NO$_y$ at the Jungfraujoch during selected field campaigns.
nitrate to total NO$_y$ during synoptical lifting can be explained by wet deposition. The period between March 27 and April 2, 1998 (Fig. 4.9c) was characterized by clean conditions till the morning of March 30. During this period, an average NO$_y$ mixing ratio of 350 ppt was observed with PAN (39%) as the most abundant NO$_y$ species, followed by NO$_x$ (24%) and inorganic nitrate (4%). Thermally induced vertical transport occurred on the three following days, where very high NO$_y$ mixing ratios were found. On the first day, a maximum NO$_y$ concentration of 3.3 ppb was observed. During this peak event, NO$_y$ consisted mainly of PAN (42%), followed by particulate nitrate (13%), NO$_x$ (9%) and HNO$_3$ (3%). In the following night, the air was replaced by undisturbed FT-influenced air, and low concentrations were observed. A very high injection of NO$_y$ was then observed on March 31 with a maximum concentration of 6.9 ppb, which consisted mainly of particulate nitrate (52%), PAN (30%) and NO$_x$ (5%). HNO$_3$ was below the detection limit during this episode, indicating that the formation of particulate nitrate was favored due to neutralization of HNO$_3$. The NO$_y$ rich air was again replaced through horizontal advection during the following night. On April 1, another thermally induced injection was observed. The NO$_y$ mixing ratio reached 4.7 ppb, and consisted mainly of PAN (34%), followed by particulate nitrate (20%), NO$_x$ (10%) and HNO$_3$ (1%). However, the following advection of clean air was not effective enough to replace the injected air mass completely by FT air, leading to elevated NO$_y$ mixing ratios during the night of April 2. This phenomenon was already observed during summer 1997 for convective days with low wind speed at the 500 hPa level (see Chapter 3.3). The period from April 3-17, 1998 was characterized by several south-fohn episodes accompanied by high NO$_x$ concentrations (see Fig. 4.8).

**Seasonal variation of the NO$_y$ level and speciation**

Transport of aerosol particles to high alpine sites occurs mainly during the spring and summer months. Thermally induced vertical transport seems to be the most important mechanism for upward transport of aerosol particles at the JFJ [e.g. Lugauer et al., 1998]. Other potential transport mechanisms (frontal systems, fohn) are less important for particle related parameters, and they were often accompanied by a decrease of the aerosol surface area.
concentration (see above). However, synoptical lifting and föhn winds can be important for the upward transport of gaseous compounds.

Figure 4.10 shows the levels and speciation of NO$_y$ during selected periods. The NO$_y$ mixing ratio remained relatively constant during undisturbed FT periods. Highest NO$_y$ mixing ratios were observed during spring, but the seasonal difference between summer and winter was small. However, differences can be seen in the NO$_y$ speciation.

![Diagram of NO$_y$ levels and speciation for selected periods](image)

Fig. 4.10: NO$_y$ levels and speciation for selected periods:

1. winter, undisturbed FT, 12 - 13 Feb 1998
2. summer, undisturbed FT, 27 - 30 Jul 1997, 0300-0900
4. summer, influenced by thermally induced transport, 27-30 Jul 1997, 1500-2100
5. winter, influenced by synoptical lifting, 22 - 24 Feb 1998
7. summer 16-22 Aug 1997, convective days with low wind speed at the 500 hPa level [Zellweger et al., 1999]
8. spring, south foehn, 14 Apr 1400 - 16 Apr 1600, 1998
9. spring, influenced by thermally induced transport, 30 Mar 2 - 2 Apr 1998, 1500-2100
The NO$_x$/NO$_y$ ratio was highest during winter (0.46) and lowest during spring (0.21). This reflects the lower photochemical activity during the winter months. By similar reasons, PAN/NO$_y$ was highest during spring (0.39) and lowest during winter (0.20). Meteorological processes also have a strong influence on the level and speciation of NO$_y$. The NO$_y$ speciation for selected periods (thermally induced vertical transport, fohn, frontal systems) is also shown in Fig. 4.10. The NO$_y$ mixing ratio reached an average level of 1 to 4 ppb, a factor 4 to 10 higher compared to undisturbed FT conditions. The NO$_x$/NO$_y$ ratio was lowest during episodes with thermally induced vertical transport, accompanied by high NO$_3$/NO$_y$ and PAN/NO$_y$ ratios. This again reflects the photochemical transformation of NO$_x$ during thermally induced upward transport. The low NO$_x$/NO$_y$ ratio (usually <0.20) suggests that the transport is a multi-step process, with a residual layer of photochemically aged air formed over the Swiss plateau in a first step. In a second step, photochemically aged air is then lifted to the JFJ through thermally induced vertical transport. The low NO$_x$/NO$_y$ and the high PAN/NO$_y$ ratios also suggest that PAN degradation is not a major source of NO$_x$ at the JFJ. Rather, the Alpine region appears to be a passive transport pathway of PAN (and other NO$_y$ compounds), which is in line with recent results from FREETEX'98 [Carpenter et al., 2000].

**Export of reactive nitrogen species to the free troposphere due to mountain venting**

Although fohn events can be an important mechanism for the vertical transport of several NO$_y$ compounds to the JFJ, significant export of these species is not expected due to the descent of airmasses leeward of the JFJ. In contrast, thermally induced vertical transport over mountainous terrain, or mountain venting, may contribute to the export of CBL airmasses into the FT [Kossmann et al., 1999]. Recent airborne lidar measurements over the JFJ in July 1997, illustrated that the CBL height reached 4000 - 4100 m asl through thermally induced vertical transport [Nyeki et al., 2000]. Water mixing ratios from radiosonde data indicated that the subsequent advection of these air masses resulted in the formation of a residual layer, from ~ 2000 - 4000 m asl, leeward of the Alps, and suggest the mountain venting of CBL gases and
aerosols to the FT.
An estimate of the PAN mass concentration vented into the lower troposphere was made with a simple box model during field campaigns from July 30 - 31 1997 and March 31 1998. PAN was chosen because it is an important reservoir compound of NO\textsubscript{y} in the upper troposphere. Dimensions of the residual aerosol layer were estimated as follows. Depth was taken from radiosoundings north (Payerne, CH; Munich, Germany) and south of the Alps (Milan and Udine, Italy). A detailed analysis of water-vapor mixing ratios from radiosoundings revealed the presence of residual layers, leeward of the Alps, which may be attributed to mountain venting [Nyeki et al., 2000]. Average leeward residual layer depths on July 30-31, 1997 and March 31, 1998 were 1850 ± 550 m (1σ) and 1650 ± 100 m (1σ), respectively. The horizontal extent was estimated from the existing width of the Alps (100 km) plus that due to advection. The latter was calculated from the duration of CBL conditions (1400 to 1800 CET according to diurnal variations of aerosol parameters, NO\textsubscript{y} and PAN) and the average windspeed at 3000 to 4000 m asl. The windward breadth of the Alps was estimated at 630 ± 50 km.

Only specific days that exhibited a clear residual layer, leeward of the Alps, were considered. Results gave a PAN export of 0.36 ± 0.13 (1σ) Gg day\textsuperscript{-1} for July 30 - 31, 1997 and 1.06 ± 0.22 (1σ) Gg day\textsuperscript{-1} for March 31, 1998, which corresponds to fluxes of ~ 5.6 kg km\textsuperscript{-2} day\textsuperscript{-1} and 16.9 kg km\textsuperscript{-2} day\textsuperscript{-1} over the Alps. This may be put into context by considering that i) the above July days occurred during a 36-day field campaign (July 18 - August 23) and the above March day during a 15-day campaign from March 20 - April 4, and ii) that thermally induced vertical transport occurred with an annually averaged frequency of 21% (April 97 to March 99 period). Mountain-induced venting may therefore be an important source of not only reactive nitrogen but also of aerosols to the regional FT under certain synoptic conditions. This may have an important influence on tropospheric chemistry, since the atmospheric lifetime of e.g. PAN increases significantly in the higher and hence colder parts of the troposphere. This enables long-range transport to more remote areas of the troposphere, and decomposition of PAN may finally influence photochemical ozone production. The fact that large-scale NO\textsubscript{x} plumes were observed in the upper troposphere downwind of frontal systems [Brunner et al., 1998] also provides strong evidence
that frontal systems are an important export mechanism. However, this export is more difficult to quantify due to the absence of stable layers. The fact that increased mixing ratios of NO\textsubscript{x} and PAN were observed at the JFJ during synoptic lifting also suggests that frontal systems vent planetary boundary layer (PBL) air into the free troposphere. During the autumn and winter months, this process can become the dominant exchange mechanism between the PBL and the FT. However, aerosol particles are subject to scavenging processes, which may explain the larger seasonal variation of many aerosol parameters compared to gaseous compounds.

### 4.4 Conclusions

Speciated and total NO\textsubscript{y} were measured at the high-alpine site Jungfraujoch (JFJ) over a two-year period. It was shown that NO\textsubscript{y} mixing ratios and partitioning strongly depend on meteorological conditions. Meteorological filters were used to distinguish between undisturbed and disturbed FT conditions. The meteorological processes which were identified to influence NO\textsubscript{y} mixing ratios and composition include föhn (both north and south), synoptical lifting (e.g. fronts) and thermally induced vertical transport. Characterization of these processes is an important aspect in understanding tropospheric chemistry in the Alpine region. The filters used for this study were based on meteorological parameters with the exception for thermally induced vertical transport where a combination of the Alpine weather statistics and the diurnal variation of certain species (NO\textsubscript{y}, aerosol surface area concentration, and specific humidity) was used. Highest NO\textsubscript{y} mixing ratios were observed during föhn events. This is in contrast to aerosol parameters, for which thermally induced vertical transport is the major process for upward transport. Seasonal variation in the composition of NO\textsubscript{y} was found, with PAN being dominant during spring and summer, and NO\textsubscript{x} during autumn and winter. Finally, an estimate of PAN export to the FT through thermally induced vertical transport was made. It was shown that significant quantities can be vented into the FT, and hence result in long-range transport of reactive nitrogen reservoir species.
4.5 References


5. Summary and Outlook

Measurements of total NO\textsubscript{y} were performed over a two-year period at the Jungfraujoch (JFJ) high-alpine research station. In addition, seasonal campaigns of speciated NO\textsubscript{y} were performed to investigate NO\textsubscript{y} partitioning at the JFJ. Since one emphasis of measurements at the JFJ was to examine the influence of meteorological transport processes on the tropospheric chemistry over the Alpine region, care was taken to identify and separate periods that were potentially perturbed by local or regional pollution sources. This was carried out with meteorological filters, which were used for the first time at a high-alpine site to distinguish between undisturbed free tropospheric (FT) and disturbed FT conditions. Several meteorological processes (i.e. föhn events, synoptical lifting, and thermally-induced vertical transport) were shown to have a strong impact on the NO\textsubscript{y} level and speciation at the JFJ. Data analysis with respect to different meteorological situations therefore allows to study the undisturbed FT over the Alpine region. The JFJ measurements substantially add to the European database of NO\textsubscript{y} and constituent species, as most previous NO\textsubscript{y} studies have been conducted at sites in North and South America in addition to some work over the Pacific Ocean and Hawaii.

Instrumental aspects

The measurement techniques for NO\textsubscript{y} and constituent species allowed their concentrations to be accurately determined in the relatively clean environment at the JFJ. However, it should be noted that some of these techniques can suffer from artifacts under different environmental conditions, which will be discussed in the following.
Performance of the WEDD/AC system

The wet effluent diffusion denuder / aerosol collector (WEDD/AC) system has been operated in other field campaigns since the JFJ experiment. For example, aerosol measurements were performed in early summer of 1998 in the suburbs of Milan as a part of an internationally coordinated field campaign run under the auspices of EUROTRAC-2. A comparison of the WEDD/AC with filter pack measurements showed very good agreement for particulate nitrate up to concentrations of 20 μg m\(^{-3}\) [Streit et al., 1999]. On the other hand, HONO values have shown differences between the DOAS and WEDD/AC techniques, with the latter usually being 100-200 ppt higher. The reason for this has so far not been clarified. Numerous investigations of possible artifacts by uptake of gaseous NO\(_2\) in other WEDD devices have been made, and have shown to produce negligible artifacts. However, these studies have usually been performed with synthetic air. Recent measurements with the WEDD/AC in a smog chamber with freshly emitted diesel soot gave some evidence that the NO\(_2\) interference in WEDD/AC devices strongly depends on the presence of other pollutants. Lee and Schwartz [1983] reported an enhanced NO\(_2\) uptake in S(IV) containing water, with a pH-dependent first order reaction both in NO\(_2\) and SO\(_2\). It is therefore to be expected that the NO\(_2\) interference in WEDD devices might be enhanced by the presence of SO\(_2\). Preliminary results from laboratory studies showed that the NO\(_2\) interference may be significantly higher (>1% of gaseous NO\(_2\)) in the presence of 20 ppb SO\(_2\) [L. Gutzwiller, personal communication]. Therefore, care must be exercised when drawing conclusions from HONO measurements performed with WEDD devices in polluted environments.

Further investigations are needed to investigate to what extent these laboratory results are applicable to field experiments and if other interfering species may cause additional HONO artifacts.

Performance of the NO/NO\(_x\)/NO\(_y\) system

The Au catalyst showed good performance at the JFJ, with conversion efficiencies being above 95% for NO\(_2\). However, it should be noted that converter poisoning may become a problem in more polluted environments.
Sea salt aerosols are known to lower the conversion efficiency of this converter type, and frequent cleaning is necessary for measurements in a marine environment.

The sensitivities of the CLDs used at the JFJ were not sufficient to detect the very low NO mixing ratios of a few ppt. It is therefore planned to renew the CLDs and to replace the photolytic converter.

**Importance of the study to future measurements at the JFJ**

To know the meteorological processes which influence the concentrations of different species at a measurement site is of great importance. Station-specific filters were used for the investigation of NO$_y$ and its constituent species for the first time at a high-alpine site. NO$_y$ species are well-suited to study different meteorological influences, because they cover aspects of water-soluble gases (e.g., HNO$_3$) and aerosols (e.g., NH$_4$NO$_3$) as well as less soluble species (e.g., NO$_2$, PAN). The investigation of these meteorological transport processes is important in the following aspects:

i) **Link to source regions**

By detailed investigation of meteorological transport processes, a link to different source regions in Europe may be established. It can be shown that e.g. south fohn events result in higher NO$_x$ mixing ratios compared to north fohn at the JFJ, which may reflect different emission sources north and south of the Alps. For this purpose, further investigations including emission inventories are needed. The planned activities at the JFJ include the measurement of selected halogenated hydrocarbons and a definition of source locations with the help of trajectories.

ii) **Analysis of trends**

Long-term trend analysis of air pollutants at remote sites requires not only accurate measurement techniques, but also a detailed knowledge of the processes which influence a certain measurement site. The meteorological influences described in the present study will therefore help with the analysis of other time series, where a similar influence can be expected (e.g., ozone, halogenated hydrocarbons).
iii) Remote sensing

Future development in monitoring the composition of the atmosphere will include remote sensing techniques, such as satellite-based systems. For this purpose, surface measurement sites well-characterized with respect to meteorological influences may help with the calibration and ground-truthing of these instruments.

It is also planned to improve the station-specific meteorological filters. For instance, a specific meteorological filter which responds to all cases where thermally-induced vertical transport occurs is still not available. A combination of meteorological parameters and the diurnal variation of certain trace species (see Chapter 4) showed good results, but further improvement of this method is desirable for the interpretation of the JFJ data.
5.1 References


Publications

Several publications based on the work described above have already appeared in the literature or were submitted (peer-reviewed journals only):


Curriculum Vitae

Christoph Zellweger
born on 19 December 1964 in Uzwil, Switzerland
citizen of Teufen (AR), Switzerland

1972 - 1978 Primary school, Wil.
1981 - 1985 Gymnasium in St. Gallen, Matura Type C
1986 - 1990 Study of chemistry, ETH Zürich
Diploma thesis with Prof. Dr. D. Seebach: "Zyklische und offenkettige 3-Hydroxybuttersäureoligomere"
October 1990 Diploma in chemistry, ETH Zürich
1990 - 1991 Employment at Lever Suter, Münchwilen:
"Ökologische Beurteilung von Reinigungsmitteln"
1992 - 1995 Employment at EMPA Dübendorf,
"Schadstoffemissionen aus Baumaterialien"
since April 1996 Ph.D. student with Prof. Dr. R. Zenobi at the ETHZ, in collaboration with the Paul Scherrer Institute, Villigen, (PD Dr. U. Baltensperger) and EMPA Dübendorf (Dr. P. Hofer)

Dübendorf, December 1999